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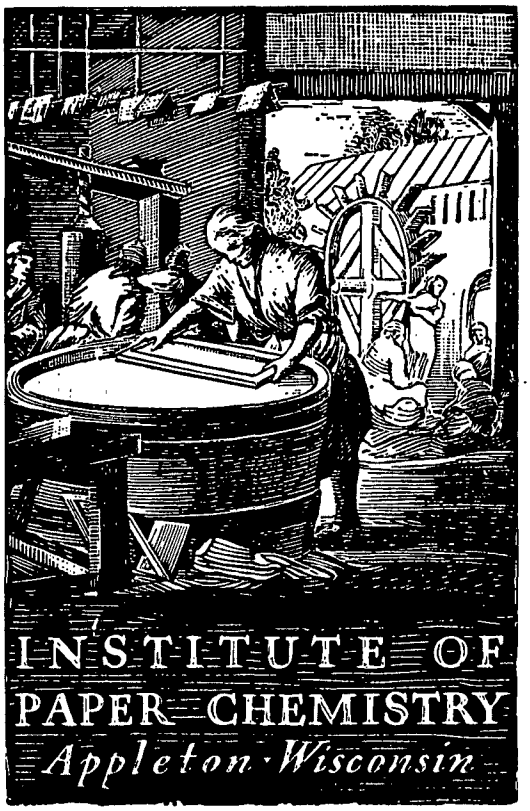




# STUDY OF THE CARBOHYDRATE PEELING AND STOPPING REACTIONS UNDER THE CONDITIONS OF OXYGEN-ALKALI PULPING

Project 3265
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Report One

A Progress Report

to

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

January 9, 1976

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## SUMMARY

A flow reactor has been constructed that will handle solutions of dissolved oxygen in alkaline systems at high temperatures and under pressure. The dissolved oxygen can be kept in solution in a system of heating and reaction coils by use of nitrogen pressure; use of this gas rather than oxygen will not alter the concentration of oxygen in solution. The concentrations of dissolved oxygen in solutions at room temperature have been measured with a Clark-type polarographic electrode, which has been modified for readings at higher oxygen pressures. The response of the electrode with higher pressures of oxygen is linear. This response has not been calibrated by chemical analysis yet but is of the order of 200 parts per million or above. The rate of solution of gaseous oxygen in aqueous solutions has been found to be a relatively slow process and the response of the electrode to high concentrations of gaseous oxygen is much faster.

Experiments studying the effect of various metals on the oxidation of carbohydrates have shown that nickel is inert as far as peroxide-promoted oxidative reactions are concerned. Therefore, the present flow reactor has been constructed with heating and reaction coils and other fittings in the reaction zone being made of nickel. Less critical parts of the reactor are of stainless steel; mixers in the reaction zone are made of Kel-F.

Analysis of preliminary oxidations of cellobiose has shown the presence of acids in the disaccharide region, diagnostic of oxidation, in contrast to acids of lower molecular weight formed by peeling. These analyses were done by gas

chromatography of the trimethylsilyl derivatives. For partially completed reactions, unreacted starting material (cellobiose) was removed by an alkaline treatment in nitrogen, leaving the disaccharide acids as stable products.

The presence of moist oxygen gas at high pressures has been found to be very corrosive to steel portions of the pressure chambers used with the flow reactor. Accordingly, these portions have been chrome-plated to prevent this adverse action.

The small concentration of dissolved oxygen in the alkaline solutions requires an equally small concentration of carbohydrate substrate. So far gas chromatography has been found to be the best method of analysis of such systems, but liquid chromatography is being explored. This will be a valuable tool if the sensitivity of the detectors can be increased.

Reaction systems are also being analyzed for peroxide formation, and a great difference has been noted between those with magnesium and with cobalt ions present.

## INTRODUCTION

Reactions of carbohydrates under pulping conditions with an alkali-oxygen system normally involve treatment of an aqueous solution or slurry in a digester with gaseous oxygen at a certain pressure. Stirring of the aqueous portion and maintenance of the oxygen pressure allow the continuous introduction of oxygen into the aqueous solution during the time of reaction. Thus, there is an excess of gaseous oxygen to replenish the dissolved oxygen that has reacted with the carbohydrate in the alkaline solution. The operation of a digester (heatup and cooling) requires a period of minutes to several hours and so kinetic data can be obtained only for relatively slow reactions, such as the breaking of a glycosidic bond.

In the present project we are interested in the two very rapid reactions, peeling of end groups from carbohydrates (oligosaccharides or polysaccharides) and oxidation of these end groups to acidic units that are resistant to peeling. For the study of such fast reactions, with reaction times as low as the millisecond range, a flow reactor is necessary. Such reactors involve the very rapid mixing of solutions to start and stop the given reaction within a short time. For an earlier cooperative project at the Institute we constructed such a reactor, and used it for a study of the peeling of end groups under alkaline conditions. Reaction times as low as 10 milliseconds were obtained at temperatures up to 170°C.

For analogous flow reactor studies in an alkali-oxygen system we must use solutions of dissolved oxygen which are mixed rapidly with carbohydrate solutions. Under such conditions we cannot supply gaseous oxygen continuously to the reaction, but must deal only with the oxygen dissolved in one of the solutions we are mixing. Therefore, a great deal of this report is concerned with a discussion

of dissolved oxygen in water and in solutions of electrolytes, with the measurement of oxygen concentrations in pressurized solutions, and with means of controlling such solutions.

Since the dissolved oxygen solutions will be confined within a pressurized system composed of various heating and reaction coils, we are also concerned with the possible catalytic effects the metals of these coils will have on the reaction. A detailed study is given of these effects and the conclusion that nickel is the most suitable metal for use in the flow reactor for the metal parts in the reaction zones.

Finally, the organic reaction systems have to be analyzed for organic products, and a technique of gas chromatography of the trimethylsilyl derivatives has been chosen. Two important factors are relevant here. First, the amount of carbohydrate substrate used in the flow reactor must be in low concentration, since the concentration of dissolved oxygen is very low even in pressurized systems. Secondly, the acidic products are separated from the unreacted carbohydrates by destroying the latter in a hot alkaline treatment, after the initial oxygen reaction. Data from the earlier project on the peeling reaction have demonstrated that such an alkaline treatment, for a given time, is essentially complete.

The flow reactor at present is ready for study of various reaction conditions; analyses will be made of the products formed from the carbohydrates and, hopefully, a measurement of the oxygen consumed in the various reaction systems.

# THE FLOW REACTOR

## INTRODUCTION

Flow reactors have been used for many years in the study of very fast biological reactions (1). Reaction times in the millisecond and microsecond ranges have been obtained. The original concept of a flow reactor depended on efficient mixing of the several reactants, so much work was done in this area (1,2). The reactions studied were confined to lower temperatures and mild reagents, and few reactions have been observed at higher temperatures.

The present section deals with the operation of a flow reactor capable of operating under pressure to 200 psi and at temperatures up to 170°C. The reactions are terminated by mixing with a quenching agent or cooling the reaction solution by mixing with an excess of cold water. In an earlier project at the Institute, reaction times down to 10 milliseconds were observed in applications to some of the fast reactions occurring in alkaline pulping systems.

The operating principle of the flow reactor is shown in Fig. 1. Reactants A and B are forced simultaneously from syringes through a mixer into a reaction zone. At a second mixer the reaction is terminated by addition of a quenching agent C. The solution is then analyzed. The reaction time $T_R$ is directly proportional to the volume $V_C$ of the reaction zone and inversely proportional to the flow rate of the liquid through this zone.

$$T_R = V_C/(\text{ml/sec}) = \text{seconds}$$

The actual operation is more complicated in that heating coils are placed between the syringes and the first mixer, and a certain period of time is allowed for thermal equilibration, before the heated solutions are pushed

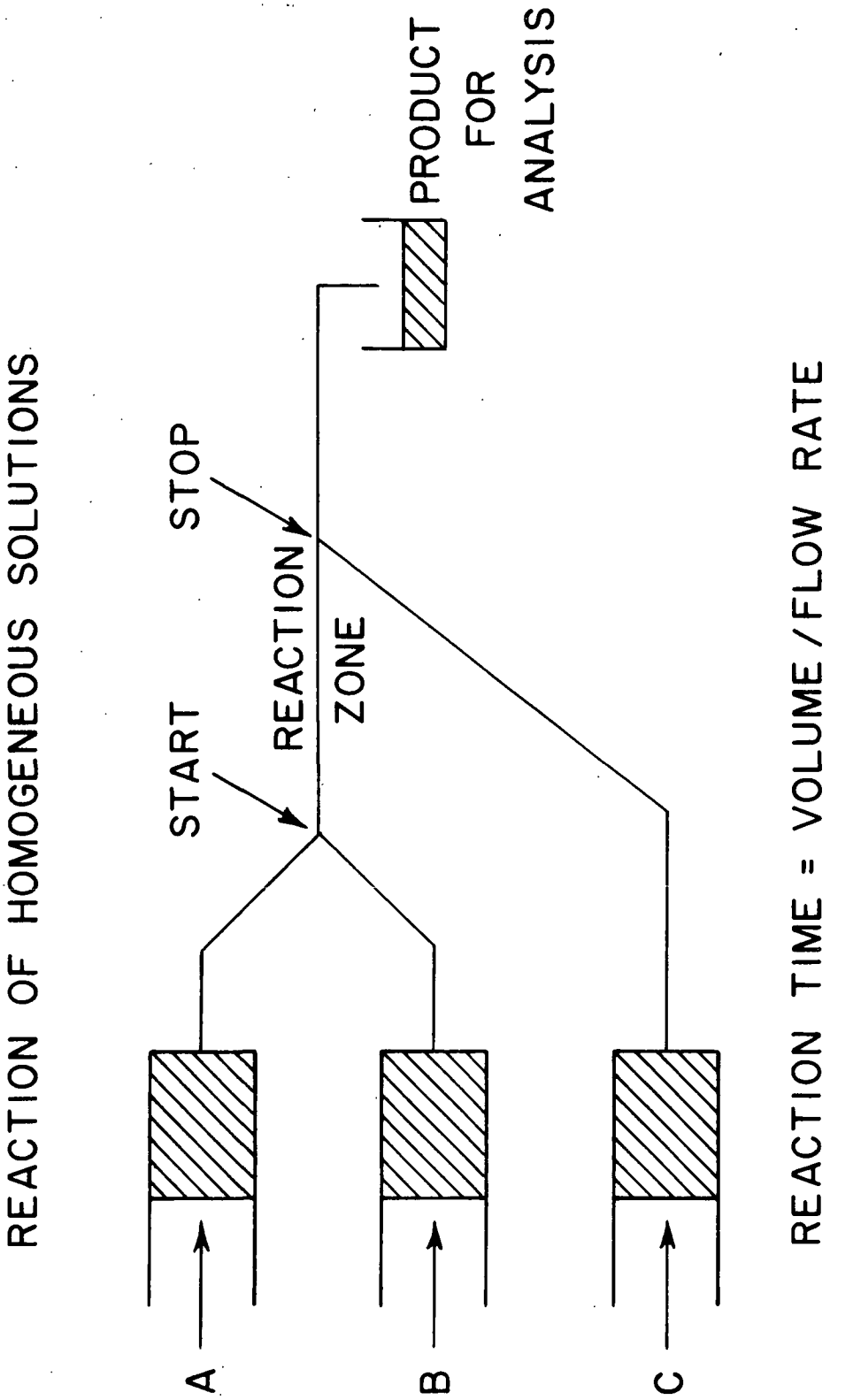


Figure 1. Reactions of Homogeneous Solutions in a Flow Reactor

continuously through the reaction zone or coil. This operation is composed of three phases.

(a) The reaction syringes (20.8 ml each) are half-emptied into the heating coils (13 ml each).

(b) After a given heating interval, the remainder of the solution in each syringe (10.4 ml) is pushed into the heating coils. This cold solution drives most of the heated solution (about 17 ml for both coils) through the reaction coil.

(c) Just before the reaction solution enters the second mixer, quench reagent is pushed out of its syringe. The final volume of reaction solution obtained, before dilution with quench reagent, ranges from 12 to 17 ml, depending on the volume of the reaction coil (5 to 0.1 ml).

The solution remaining in the heating and reaction coils has an uncertain kinetic history, so the coils are rinsed out and dried before another run is made.

The volume of the quenching agent C is large (100 ml) compared with the volume of reaction solution leaving the reaction coil. It is essential that the latter be "bracketed" by quenching reagent, so that the reaction is terminated sharply for all the reaction solution passing through the second mixer. The bracketing is controlled automatically, and is described below.

The flow rate of the reaction syringes ranges from 0.1 ml/sec to 14 ml/sec; the volume of the reaction coil, from 0.1 to 5 ml. Thus, a range of reaction times from 50 sec to 0.01 sec can be handled. All surfaces contacted by the solutions are of type 316 stainless steel, nickel, or Teflon; the heating and reaction coils are of nickel.

CONSTRUCTION OF THE REACTOR

The apparatus is shown in Fig. 2. It consists of four sections: two pressure chambers, a steel channel holding three syringes and two hydraulic rams, and an assembly of two heating coils and one reaction coil, connected by mixers mounted in metal housings. The coils and mixers in the reaction zone are fabricated of nickel; the syringes, valves and pressure chambers are of stainless steel. The whole assembly is operated by a switchboard shown in Fig. 3.

The reaction (mix) and quench syringes are driven by the hydraulic rams in either forward or reverse directions. The two mix syringes are mounted side by side and are driven by one ram (Fig. 4).

Originally only one pressure chamber, $C_1$, was used as a "balloon" at the end of the system, and contained the quench bottle; the pressure used (nitrogen) prevented the boiling of aqueous solutions at reaction temperatures above 100°C. Pressures up to 200 psig nitrogen were used. The hydraulic pump at the other end, operating at a maximum pressure of 1000 psig, served to seal that end of the apparatus. The syringe plungers contain several O-rings. These, the Swagelok fittings connecting the mixers and the several coils, and the valves (Whitey) are all capable of holding pressure within the system. The Swagelok fittings are easily detached for cleaning of the various components. Bulkhead fittings are used on the pressure chamber.

For the present use of dissolved oxygen an additional pressure chamber is needed for preparing high concentrations of dissolved oxygen ($C_2$ in Fig. 2). This is connected to one of the mix syringes by valve, $V_6$ (see also Fig. 5).

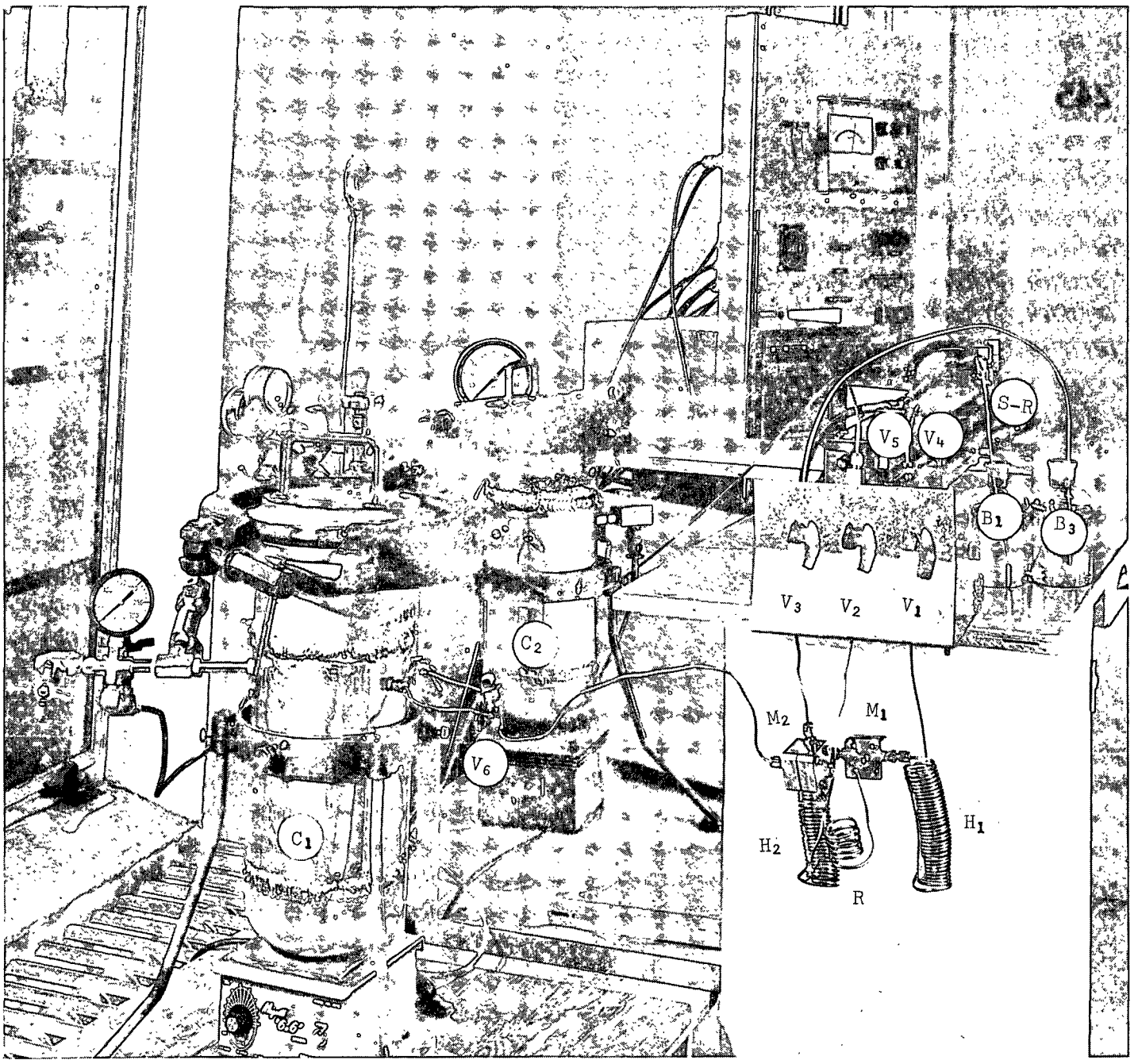


Figure 2. Flow Reactor and Pressure Chambers. $C_1$ = Nitrogen Chamber; $C_2$ = Oxygen Chamber; S-R = Syringe-Ram Assembly; $H_1$ and $H_2$ = Heating Coils; R = Reaction Coil; $M_1$ and $M_2$ = Mixers; $V_1$ and $V_2$ = Valves to Mix Syringes; $V_3$ = Valve to Quench Syringe; $V_4$ and $V_5$ = Cutoff Valves (Hidden); $V_6$ = Valve to Quench Bottle and Spill Bottle in $C_1$; $B_1$ and $B_3$ = Fill Bottles

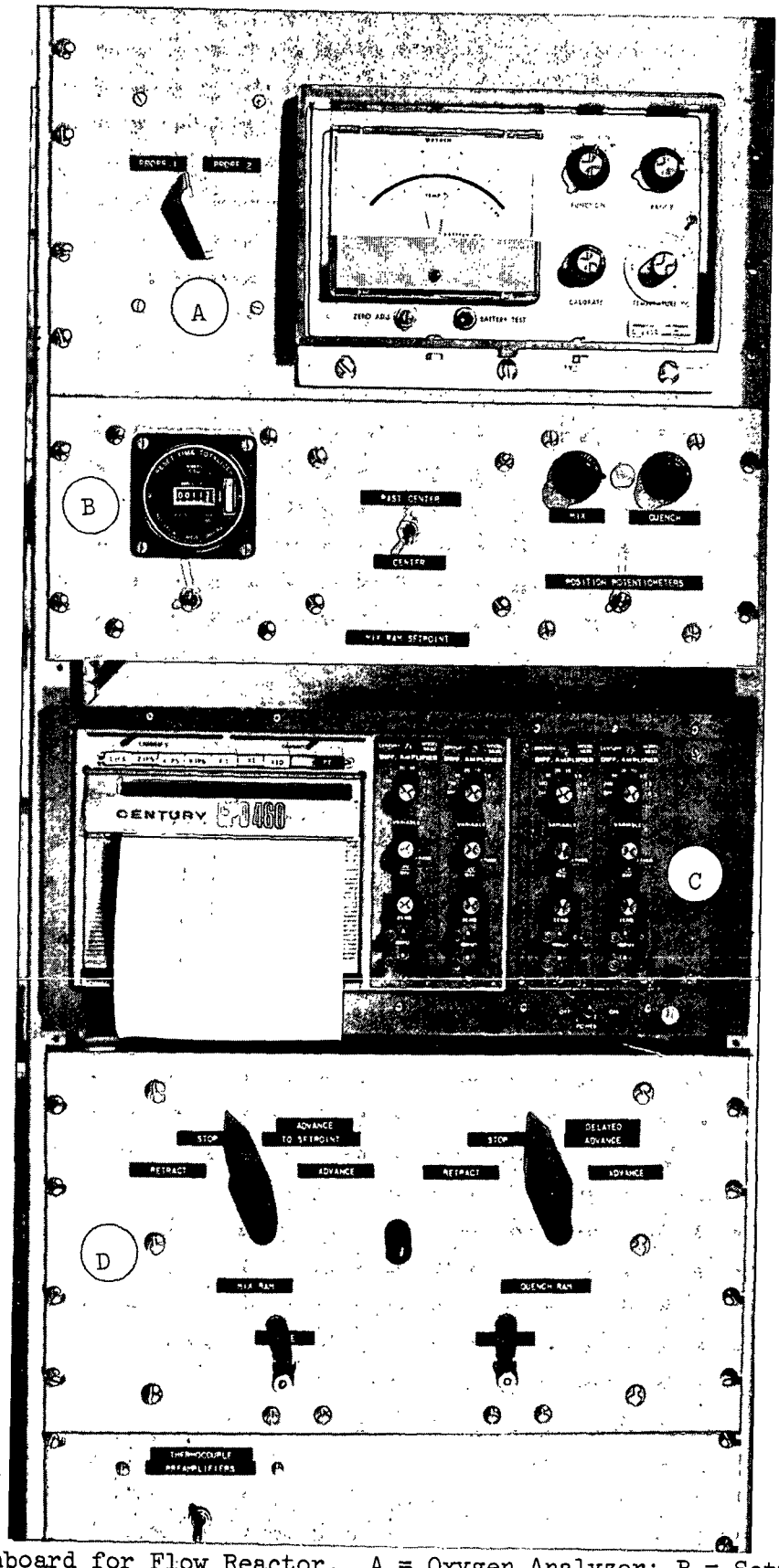


Figure 3. Switchboard for Flow Reactor. A = Oxygen Analyzer; B = Setpoint and Position Potentiometer Adjustments; C = Oscillograph Recorder; D = Regulation of Ram Movements

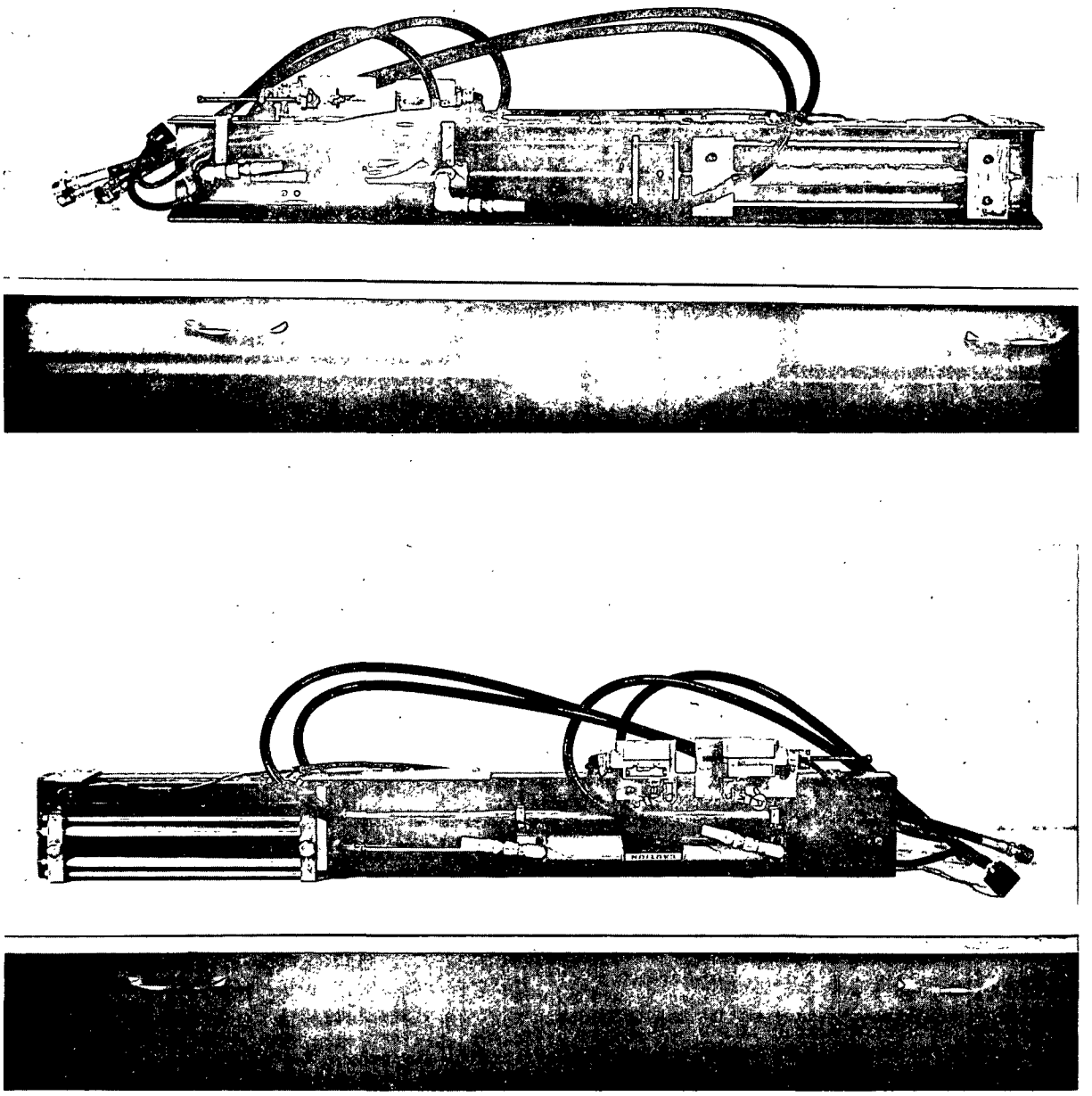

Figure 4. Assembly of Syringes and Hydraulic Rams. The Upper Picture Shows the Quench Syringe on the Right and the Ram with Oil Hoses on the Left. The Lower Picture Shows the Two Mixing Syringes on the Left and the Hydraulic Ram and Two Microswitches on the Right

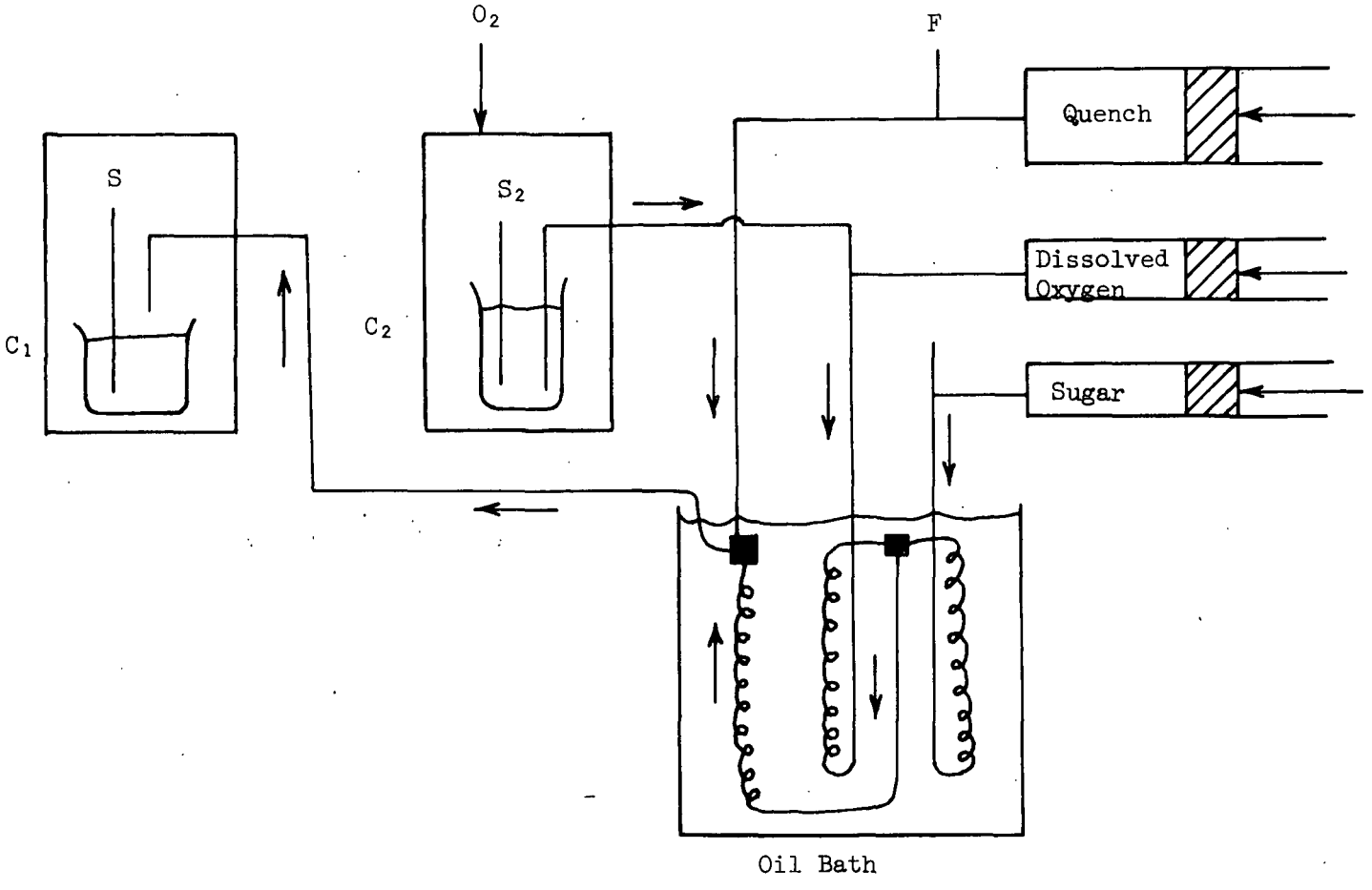


Figure 5. Direction of Flow of Liquids in Flow Reactor

The three syringes are connected to the second pressure chamber, $C_2$, to the filling bottles and to the heating coils by three-way valves, $V_1$, $V_2$ and $V_3$. When the valve handles are up, the connections are between the syringes and the filling bottles or chamber $C_2$. When the valve handles are down, the connections are made between the syringes and the heating coil (and the second mixer for the quench syringe). After a run, valve $V_4$ is a cut-off device to keep nitrogen pressure in the coil system from entering the fill bottle. Similarly, valve $V_5$ is closed during preparation of dissolved oxygen in chamber $C_2$. Valve $V_6$ is connected to a quench bottle in chamber $C_1$ and also to a "spill bottle" to collect extra liquid after the pressure in $C_1$ is relieved.

Each of the pressure chambers is equipped with a pressure-tight electrical connection so that an oxygen sensor can be connected inside the chamber to the switchboard (see Fig. 6). This is described in more detail in a later section on Dissolved Oxygen.

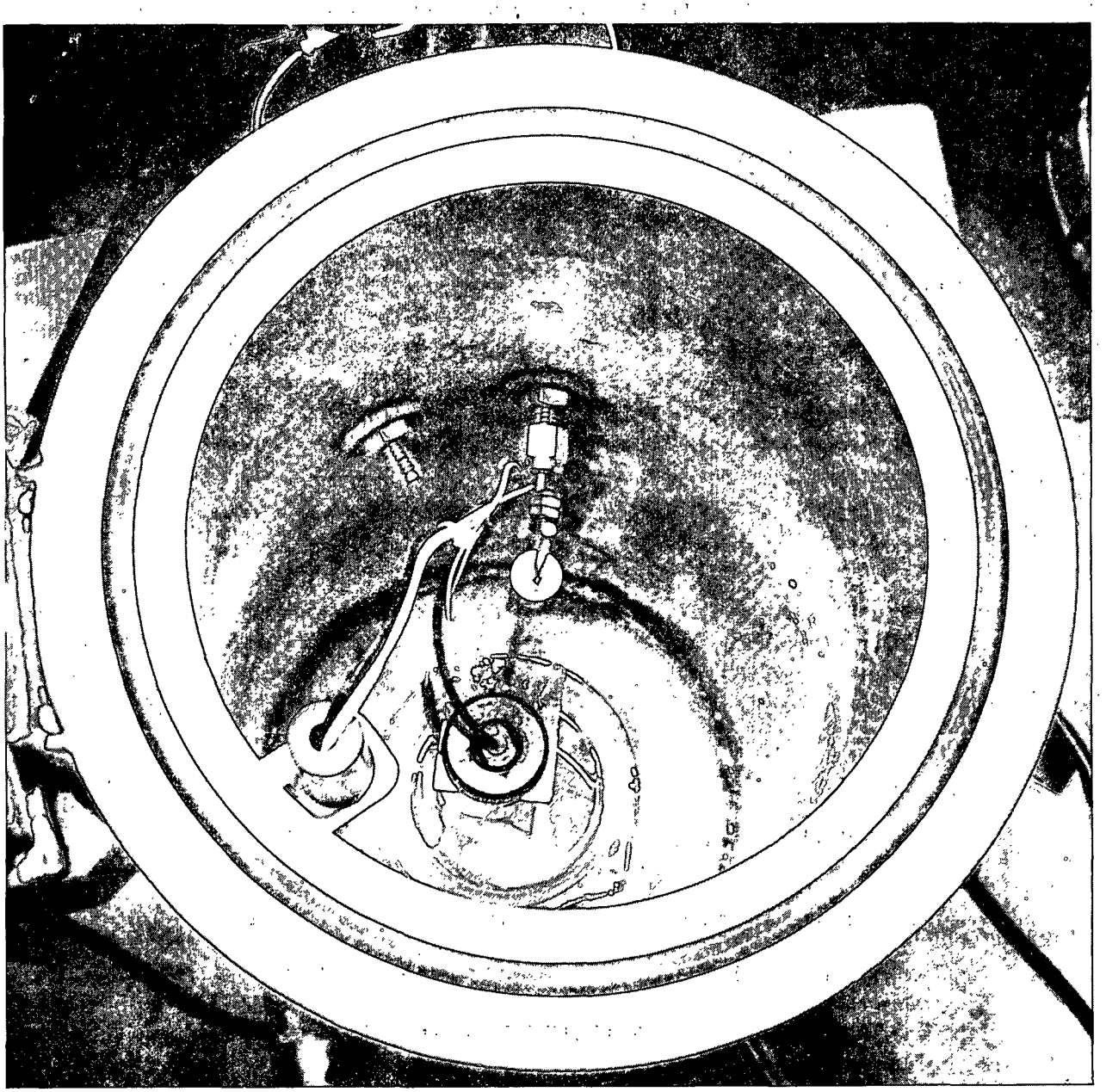

Figure 6. Top of Digester, Showing Oxygen Probe

The pressure chambers are made of stainless steel, 6 inches inside diameter, and the hinged closures are of the Tube-Turn type, equipped with O-rings for sealing. These closures are of steel, and are welded to the stainless steel bodies. Originally the closures rusted quite badly in the moist oxygen atmosphere. To prevent this, they were chrome-plated, and no corrosion has been observed.

CONTROL OF SYRINGE MOVEMENTS

The movement of the stainless steel syringes is effected by hydraulic cylinders (rams) from a rack-mounted panel (see Fig. 3). Their positions are monitored on a Hathaway 460 oscillograph recorder via linear potentiometers.

The Retract position of the mix ram control switch is used for filling the syringes (Fig. 7). The Advance position will deliver 20.8 ml; the Advance to Set point will deliver 10.4 ml. The movements of the rams (and syringes) are precise; the volumes delivered will check within 0.05 ml. The output of the combined mix syringes (set by micrometer flow control of the ram speed) ranges from 0.13 to 14.2 ml/sec.*

The quench ram control switch includes an adjustable Delayed Advance position. The speed of the quench syringe delivery ranges from 1.0 to 27 ml/sec.

The automatic action of the set-point switches MS-1 and MS-2 are shown in Fig. 8. The two mix syringes are connected side-by-side to a common push bar, to which the hydraulic ram, the linear potentiometer, and the cam rod for the

*The ram movements cannot be operated by flow rates below 0.13 ml/sec; for longer reaction times the reaction is carried out in a static rather than a dynamic mode. A certain amount of liquid is pushed into the reaction coil, left there for a given period of time and then pushed out and quenched. Care must be taken with this style of operation to prevent diffusion of unreacted solution into the main reaction system.

limit switches are also attached. The geometry is such that MS-1, originally riding in a high position for the full syringe, drops at the half-way position of the ram and stops the syringe movement (see end of $T_F$ in Fig. 9). Later, during the second half-stroke $T_K$, MS-2 is turned on and initiates movement of the quenching syringe ($T_Q$). The position of MS-2 is adjustable; it is set for the time when the reaction solution enters the second mixer. This switch will trigger only when the quench ram switch is set in the Delayed Advance position (see Fig. 7), and the mix ram switch is set to Advance.

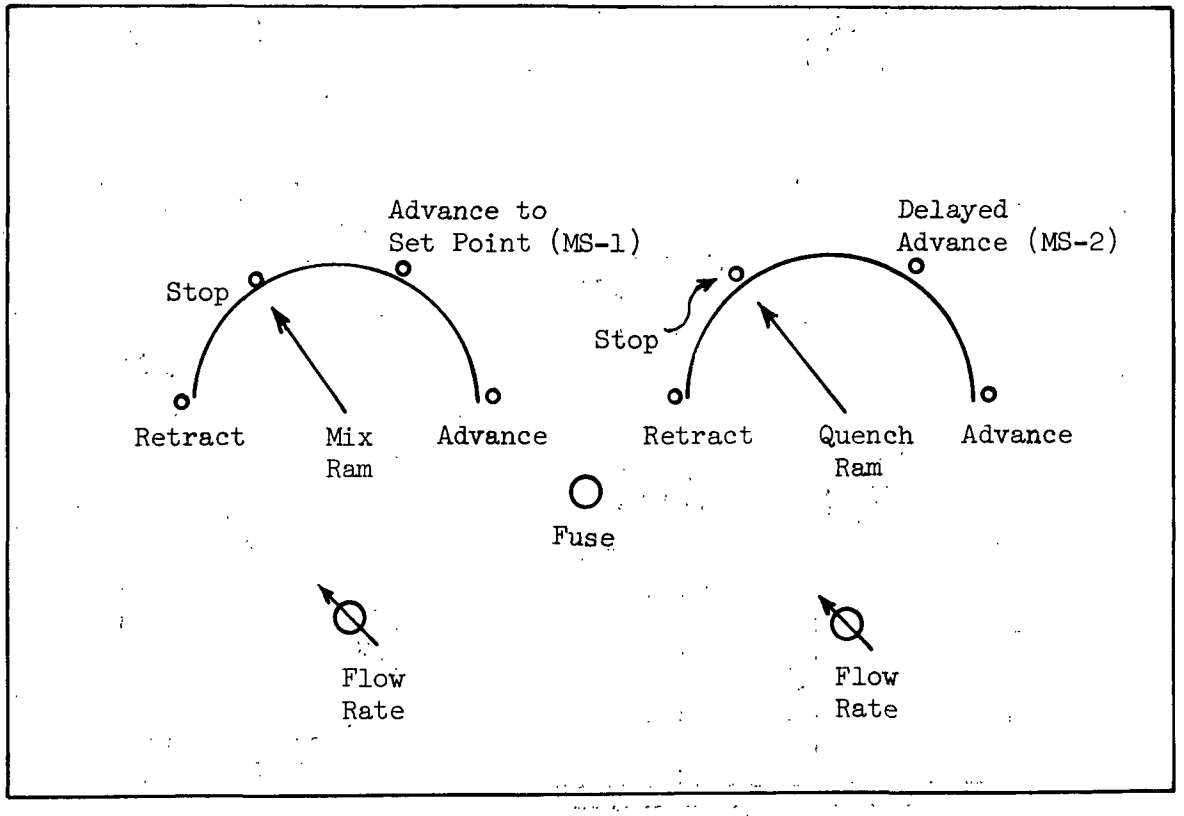


Figure 7. Manual Controls on Syringe Control Panel

The oscillograph recorder is used to measure the rate, volume and timing of liquid flow from the several syringes; this can be done to 0.01 second time. The syringe movements are shown in Fig. 9; these were taken from a recording of the signals from the two linear potentiometers.

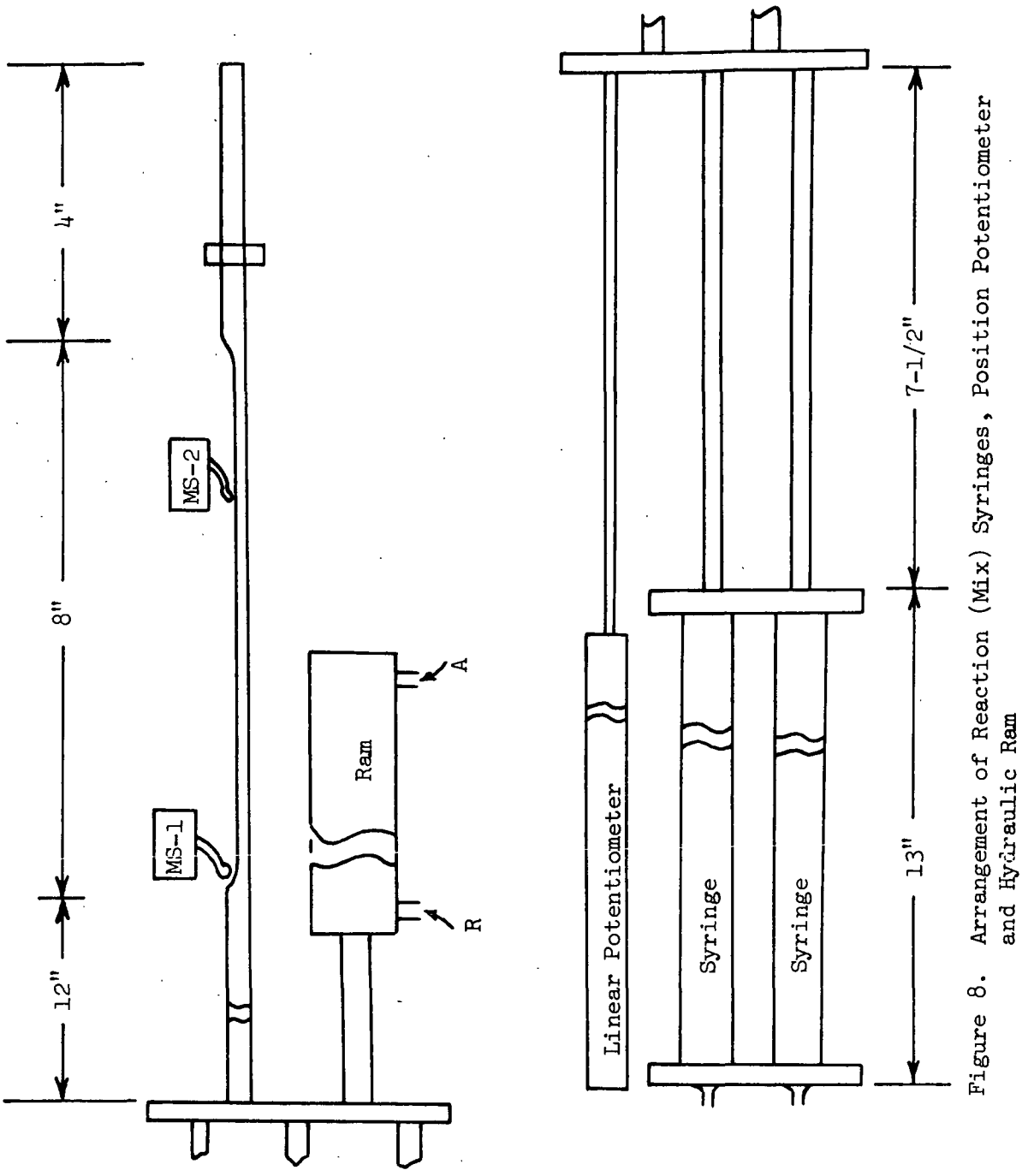


Figure 8. Arrangement of Reaction (Mix) Syringes, Position Potentiometer and Hydraulic Ram

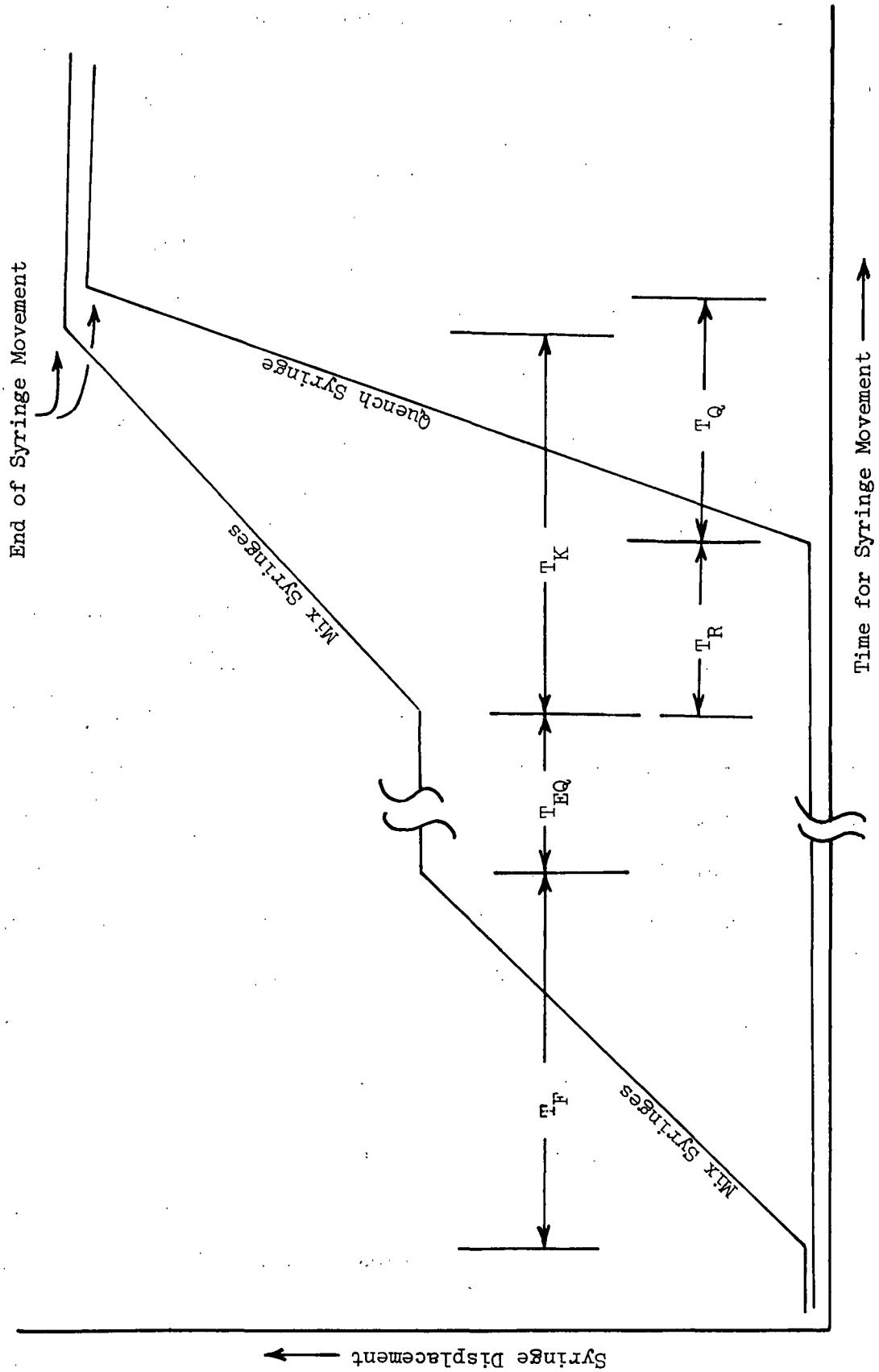


Figure 9. Oscillograph Recording of Syringe Movements

The sequence of operations during an actual run is given later.

## HEATING AND REACTION COILS AND MIXERS

The coils are made of 1/8-inch diameter nickel tubing, having a bore of 0.085 inch. The volumes of the coils were determined first by length (10.8 inches/ml) and then by connection to a reaction syringe and noting the difference in weight of liquid delivered by the latter. To prevent entrainment of air bubbles, the liquid is introduced at the bottom of the coils, both in the heating and reaction coils (see Fig. 2 and 5). The efficiency of the reactor depends on the introduction of definite volumes of liquid into the heating coils; this liquid should stop short of the mixer.

The efficiency of the reactor also depends on a maximum mixing effort with a minimum of dead volume for the mixing area. For this purpose 8-jet mixers (8 mm diameter) of the Gibson type (2) are used. They are constructed of Kel-F and mounted in nickel housings fitted with Teflon washers. The small jets (0.02 inch diameter) offer considerable resistance to liquid flow; the pressure needed from the hydraulic rams to overcome this reflects in the work done in the mixing process. The volume of two such jet mixers, with housings, and connected by a 1-inch length of tubing, 0.085 inch inside diameter, is 0.75 ml; the volume of each mixer is about 1/10 of this. Ideally the mixing should occur in a region of near zero volume, but this is difficult to obtain.

Reaction coils of volumes below 1 ml are usually short lengths of tubing of inside diameter of either 0.085 inch or 0.027 inch. With such small coils the amount of mixing occurring in the mixers becomes an appreciable factor.

MAKING A KINETIC RUN

About an hour is required to prepare the apparatus, make a run and clean up for another run. The principal steps are given below. The positions of the ram control switches (Fig. 4) are given in parentheses.

1. A solution of alkali is treated in pressure chamber $C_2$ with oxygen at 135 psig until a reading of about 240 ppm is obtained. This may take 30 minutes. The valve $V_5$ is closed during this process.

2. The two mix syringes are filled with sugar solution (via valves $V_1$ and $V_4$) and dissolved oxygen (via valves $V_2$ and $V_5$). The quench syringe is filled with cold water via valve $V_3$. (Retract.)

3. The empty coils and mixers are connected to valves $V_1$, $V_2$ and $V_3$ and to valve $V_6$ of chamber $C_1$. A quench bottle (250 ml) and a spill bottle (100 ml) are placed in the chamber, with suitable feed lines from $V_6$. The chamber is pressurized to 150 psig with nitrogen. The coils and mixers are then immersed in a container of water (the latter is raised to cover the assembly) to test for leaks of either Swagelok fittings or of Teflon washers in the mixer housings. Any faulty washers are replaced.

4. The oil bath is raised to cover the coils and mixers.

5. The valves $V_1$ and $V_2$ are turned down to connect the mix syringes to the heating coils, and then valve $V_3$ turned down to connect the quench syringe to the second mixer.

6. The heating coils are filled with the two reactants (Advance to Set Point, and quench syringe to Delayed Advance).

7. The heating coils are allowed 2-3 minutes to come to temperature in the oil bath.

8. The recorder chart is turned on, and the heated liquid forced through the reaction coil (Advance for the Mix Ram). The quenching syringe will be started automatically and will mix cold water with the reaction solution and drive it into the quench bottle.

9. The valve $V_6$ is turned to connect with the spill bottle. The recorder is stopped, the bath lowered and the coils cooled with water.

10. The pressure in chamber $C_1$ is relieved, and the quench bottle removed. The flow rates are calculated from the recorder trace and the volume of the reaction coil. The quench solution is treated with Amberlite IR-120 resin to remove alkali. The resultant solution has a pH of about 3.5, and is worked up for analysis by gas chromatography.

11. A small volume of liquid will be found in the spill bottle. This is forced out of the reaction coil by dissolved oxygen when the nitrogen pressure is removed.

12. The coils and mixers are removed, rinsed with water and acetone, and dried.

There are also other steps to check the flow controls, correct positions of the valves, etc. The several operations are rather complicated, and we have found it best to have a detailed check list to follow for each run.

# PREPARATION AND CONTROL OF DISSOLVED OXYGEN

## INTRODUCTION

Oxygen has a limited solubility in water, being of the order of 0.001 millimole per milliliter at one atmosphere oxygen pressure and a temperature of 25°C. The solubility is affected by three factors: (a) It increases with the external pressure of oxygen (Henry's Law). (b) It decreases with increasing temperature up to 100-120°C, and then increases above this temperature. (c) It decreases with increasing electrolyte concentration. The last two effects are shown in Fig. 10 and Table I.

The minimum in temperature change seems to occur in the vicinity of 100°C for all the electrolyte solutions and may be a property of water rather than of the ions present. No data are available at present for buffer solutions, such as sodium carbonate-bicarbonate.

It is unfortunate that the solubility minimum occurs around 100°C, as we will be working with temperatures from 50 to 120°C. This means we will have to take precautions with dissolved oxygen solutions prepared at room temperature, so that oxygen does not bubble out when the solutions are pushed into heating coils of the flow reactor.

The concentration of dissolved oxygen can be increased of course by increasing the oxygen pressure above the solution. The data in Fig. 10 were calculated from the respective Bunsen coefficients (solubility in ml gas/ml liquid × atm) (3) and are given for one atmosphere oxygen pressure. With a pressure of 200 psig (about 14 atm) and using the minimum of 1.5N sodium hydroxide at 100°C (Table I, 0.000425) we may be able to work with an oxygen concentration of $14 \times 0.0004 = 0.0056$ millimoles per milliliter.

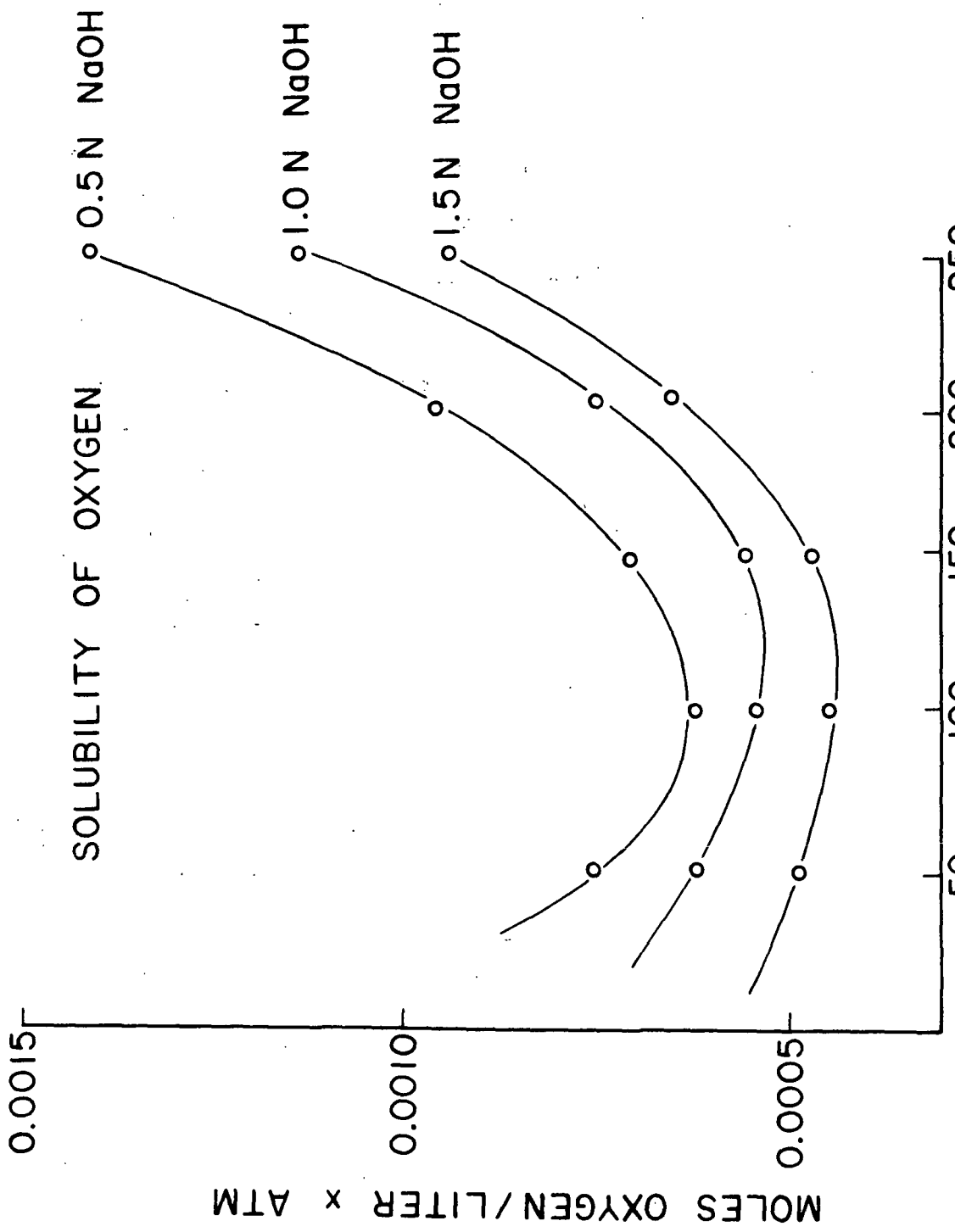


Figure 10. Effect of Temperature and Electrolytes on Dissolved Oxygen

TABLE I

SOLUBILITY OF OXYGEN IN AQUEOUS SOLUTIONS

| Solution | Solubility in Millimoles/ml at Various Temperatures for 1 Atm Pressure | | | | | |
|---|---|---|---|---|---|---|
| | 25°C | 50°C | 100°C | 150°C | 200°C | 250°C |
| Water | 0.00135 | 0.000932 | 0.000758 | | | |
| 0.5N NaOH | | 0.000755 | 0.000610 | 0.000714 | 0.000951 | 0.001409 |
| 1.0N NaOH | | 0.000605 | 0.000535 | 0.000546 | 0.000757 | 0.001143 |
| 1.5N NaOH | | 0.000492 | 0.000425 | 0.000469 | 0.000699 | 0.000927 |
| 0.5N $H_2SO_4$ | | 0.000829 | 0.000669 | 0.000763 | 0.001043 | 0.001503 |
| 1.0N $H_2SO_4$ | | 0.000767 | 0.000617 | 0.000689 | 0.000978 | |
| 1.5N $H_2SO_4$ | | 0.000714 | 0.000537 | 0.000648 | | |
| 2.87N $NH_4OH$ | | 0.000903 | 0.000700 | 0.000855 | | |
| 5.63N $NH_4OH$ | | 0.000851 | 0.000702 | 0.000816 | | |
| 8.28N $NH_4OH$ | | 0.000821 | 0.000655 | 0.000785 | | |
| 0.25N $(NH_4)_2SO_4$ | 0.001106 | 0.000829 | 0.000665 | -- | -- | |
| 0.75N $(NH_4)_2SO_4$ | 0.000869 | 0.000660 | 0.000584 | 0.000637 | -- | |
| 1.50N $(NH_4)_2SO_4$ | 0.000593 | 0.000424 | 0.000366 | 0.000386 | 0.000553 | |
| 3.0N $(NH_4)_2SO_4$ | 0.000361 | 0.000321 | 0.000223 | 0.000293 | 0.000362 | |

Note: Data for electrolyte solutions taken from Ref. (3).
Data for water estimated from graph given in Ref. (6).

According to Seidell (4) the "solubility may for practical purposes be considered a linear function of the absolute pressure." Thus, Frolich, et al. (5) determined the solubility of oxygen in water at 25°C from 0 to 70 atm pressure and obtained the linear equation, $y = 0.028x$, where $y$ is the volume of oxygen per unit of liquid, and $x$ is the absolute pressure in atmospheres. In contrast, Pray, et al. (6) found an increase of 2.25 times solubility for a pressure change from 100 to 200 atmospheres.

All these data for high pressure concentrations of dissolved oxygen were obtained at equilibrium conditions, by rocking an autoclave containing aqueous solutions or water with gaseous oxygen. This was the procedure followed by Bruhn, et al. (3), by Frolich, et al. (5) and by Pray and coworkers (6). In our present

work we used a stationary pressure chamber and agitated the aqueous solution with a magnetic stirring bar. The rate of solution under these conditions, based on readouts with an oxygen sensor, takes 10 to 20 minutes to achieve equilibrium. The response of the sensors in gaseous oxygen is very rapid, so the rate of solution must be the limiting factor. Adeney and Becker (7) have studied the rate of solution of atmospheric oxygen in solution. In our limited experience we have found that oxygen is removed from aqueous solutions (by decreasing the external pressure) far more rapidly than it is dissolved.

## DETERMINATION OF CONCENTRATIONS OF DISSOLVED OXYGEN

The Beckman Oxygen Analyzer used in our work has three parts: a Fieldlab Analyzer or readout instrument, mounted on the switchboard (Fig. 3), and two sensors or probes; the oxygen is electrochemically reduced by the latter. The sensors are usually mounted in the pressure chambers (see Fig. 6) and are connected by electrical cables to the switchboard.

The Analyzer on the switchboard has a dial reading three ranges of dissolved oxygen: 0-25, 0-10 and 0-1 ppm*. Since, in our work, much higher concentrations of dissolved oxygen are being measured, an attenuator has been installed. This was done by installing a small toggle switch on the readout panel so that appropriate range-changing resistors can be switched in (for the new ranges) or out (for the original ranges) as desired. The attenuator reduces the current at the cathode of the sensor by a factor of 100 times; thus, the dial of the Analyzer will now read also in the ranges of 0-2500, 0-1000, and 0-100 ppm dissolved oxygen.

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*32 ppm oxygen = 32 mg/liter = 1 millimole/liter = 0.001M concentration;
1 ppm = 0.0312 millimole/liter = 0.0000312M concentration.

Each probe (Beckman No. 39552 Oxygen Sensor) has eight parts, as shown in Fig. 11. The two main parts are the cathode-anode assembly, and the outer body which contains a potassium chloride electrolyte solution. The outer body is terminated at its lower end by a Teflon membrane, a retaining ring and a sensor cap. (The BOD collar is not used in the present work.) The electrolyte conducts the current between the silver anode and the platinum cathode. When oxygen diffuses through the membrane, it is electrochemically reduced at the cathode by 0.55 volt supplied from the Analyzer, mounted on the flow reactor switchboard. The membrane prevents the diffusion of unwanted electrolytes into the sensor; these may affect the readout adversely. The only gas that may affect our readouts is carbon monoxide, a possible product of the alkali-oxygen system.

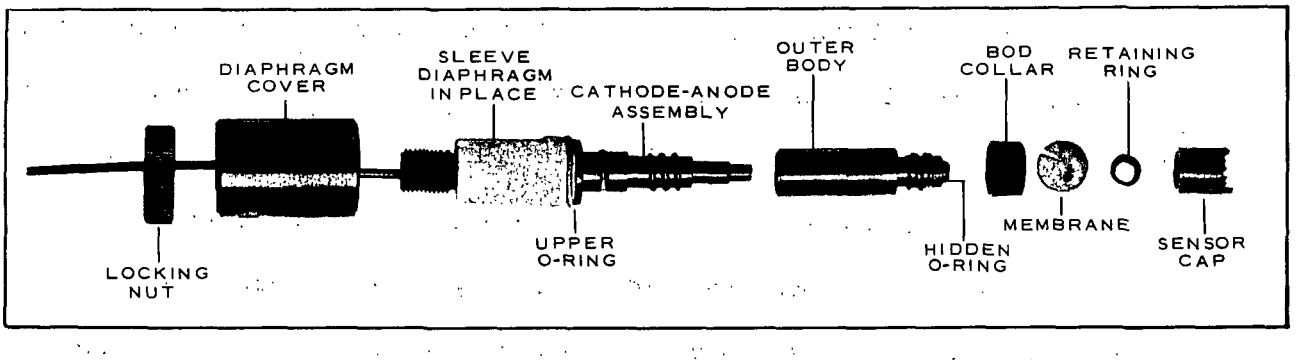



Figure 11. Disassembled Oxygen Probe

Since two probe assemblies are to be used with a single readout, a simple switching arrangement has been constructed to permit this. It is straightforward, except that provision has been made to supply the normal operating voltage of 0.55 volt to the oxygen probe not connected for readout. This should reduce considerably the time needed for stabilization after switching either probe to the readout connection.

Each probe has a Teflon membrane at the lower end of the outer body; this allows the diffusion of gaseous oxygen into the electrolyte solution near the electrodes, but prevents diffusion of interfering electrolytes. This is a typical Clark-type membrane electrode (8), except that it has a pressure compensator to prevent breakage of the fragile membrane. (See the sleeve diaphragm in Fig. 11.) The probe was designed for immersion in water at depths of 200-300 ft, but we have applied it successfully to work where pressure is from an external gaseous environment. However, it was also designed for determination of low concentrations of dissolved oxygen, and not for the high concentrations used in this project.

The probes are normally used within the pressure chamber (see Fig. 6). The electrical connections through the walls of the chambers were made with Conax type TG-20-B4-T pressure fittings. The cable of each probe was shortened so that it could be readily plugged into the inside of this pressure fitting (see Fig. 12). The external part of the probe is connected by a cable to the switchboard (see chamber $C_2$ in Fig. 2). The probes are held vertically in each chamber by a stainless steel fitting that is slipped between the locking nut and the diaphragm cover (see Fig. 11 and 12). The rod on the fitting is held in a sleeve soldered to a short piece of tubing ending in a ferrule and Swagelok nut; the latter is secured to a Swagelok (1/8 inch) bulkhead fitting mounted in the wall of the pressure chamber. The probe can be raised or lowered by adjustments of collars adjacent to the sleeve.

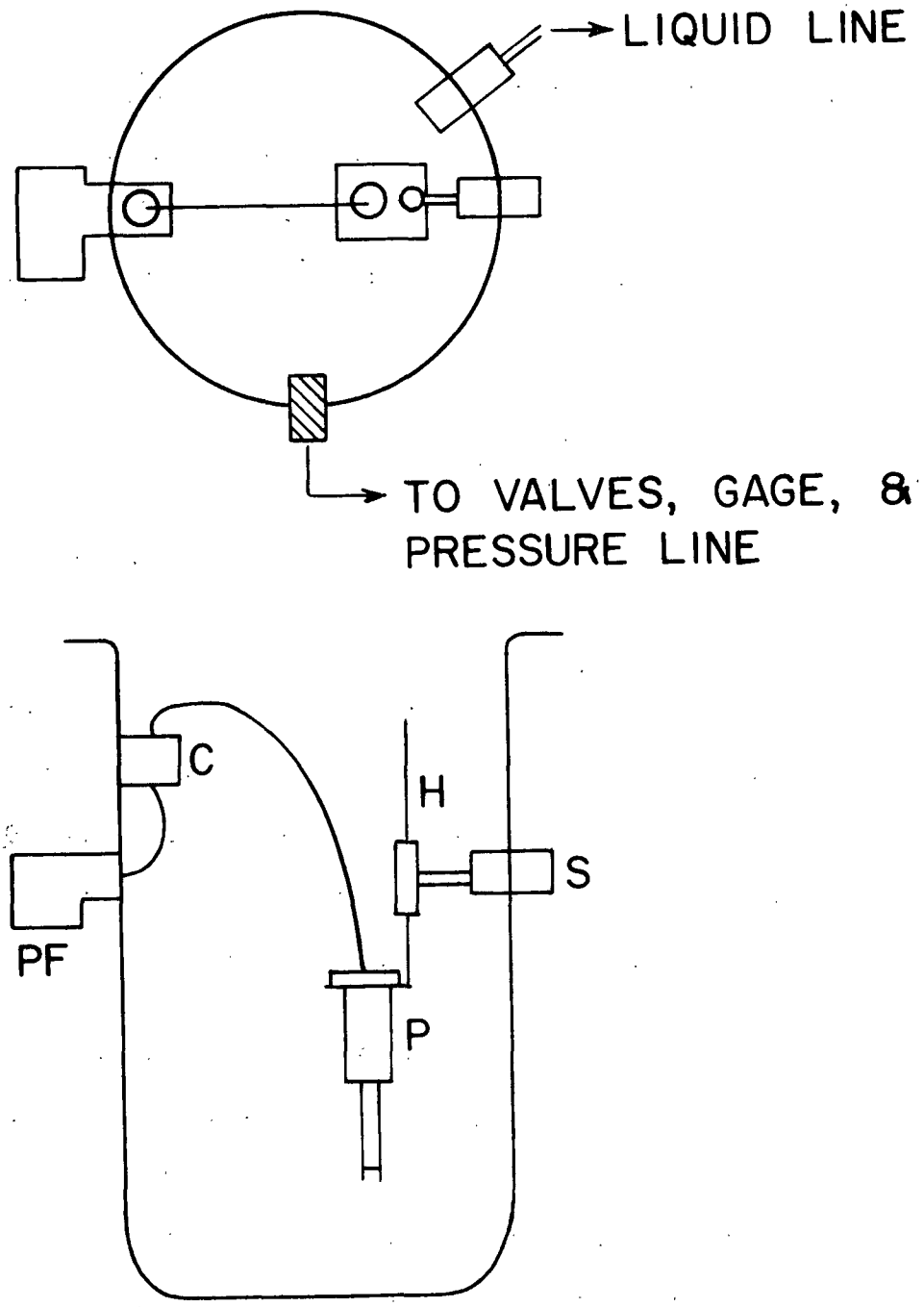



Figure 12. Pressure Connections and Holder for Oxygen Probe

CALIBRATION OF THE PROBES

The probes are normally calibrated by readings in air. The temperature is noted, and the calibration knob on the Analyzer adjusted to a given value, supplied in standard tables (see Table II). The temperature is read near the probe, on a thermistor; a readout dial is supplied on the Analyzer for this purpose.

The original thermistor temperature sensor was not in the oxygen probe, but was embedded in a brass block at the connector that was removed. So a new thermistor probe (YSI type 44115) has been attached with suitable leads to the new probe connector so that it may be immersed in the test solution alongside the oxygen probe.*

The probes can also be calibrated by immersion in water saturated with air; the reading should be identical with readings made in air alone. Calibration can also be made by a chemical analysis, i.e., the Winkler method (9). This latter method consists of oxidation of manganous hydroxide by the dissolved oxygen, addition of potassium iodide and titration of the liberated iodine with thiosulfate.

So far in the present work the probes have been calibrated in two stages: (a) in air at 8-10 ppm, and then (b) in an aqueous solution under one atmosphere of oxygen at 40-50 ppm. The probe is suspended in the solution, equipped with a magnetic stirring bar, in a pressure chamber, and the latter closed and flushed 5 times with oxygen (up to 60 psig, then back to 0 psig or 15 psia for each step). With the chamber now containing essentially 100% oxygen at one atmosphere (0 psig or 15 psia), the probe is calibrated according to Table II. This is an arbitrary calibration, but it is being used at present until chemical analyses are carried out at the higher dissolved oxygen concentrations.

*The original sensor, as supplied, had a heavy underwater connector for immersion in deep water. This was removed and shorter connections made.

TABLE II

AIR CALIBRATION OF OXYGEN SENSOR

| Temperature, °C | Oxygen in Air, ppm | Suggested Value for Pure Oxygen |
|---|---|---|
| 15 | 10.2 | 51.0 |
| 16 | 10.0 | 50.0 |
| 17 | 9.7 | 48.5 |
| 18 | 9.5 | 47.5 |
| 19 | 9.4 | 47.0 |
| 20 | 9.2 | 46.0 |
| 21 | 9.0 | 45.0 |
| 22 | 8.8 | 44.0 |
| 23 | 8.7 | 43.5 |
| 24 | 8.5 | 42.5 |
| 25 | 8.4 | 42.0 |

Note: Data in air are for fresh water at barometric pressure of 760 mm and oxygen partial pressure of 160 mm. We have used arbitrarily a 5x factor for the pure oxygen figures; this would correspond to an oxygen partial pressure of 152 mm in air.

A summary of the pros and cons of the oxygen sensors is given in Table III. These probes are being extended to ranges for which they were not originally designed, and more work will have to be done to evaluate them more thoroughly. One alteration that we have been considering is the use of the electrode assembly without the membrane. The purpose of the membrane is to exclude unwanted electrolytes in analysis of effluents of unknown nature. In our case we have a controlled system of known composition initially. The diffusion of oxygen through

the membrane may be a factor at higher concentrations and removal of the membrane might be beneficial. A new calibration mode would have to be used.

TABLE III

EVALUATION OF CLARK-TYPE OXYGEN SENSORS

Advantages

1. Rapid response, shown by tests in oxygen atmosphere
2. Linear response with increasing oxygen concentration
3. Quick calibration in 8-10 ppm range by exposure to air

Disadvantages

1. Calibration varies from one run to another at times
2. Different calibration settings needed for the two sensors
3. Temperature changes cause large changes in readout
4. Linear response is not rectilinear; a 10-fold increase in oxygen pressure gives about 5-fold increase in readout
5. Chemical analysis needed for calibration at high concentrations of dissolved oxygen

## MEASUREMENTS OF HIGH CONCENTRATIONS OF DISSOLVED OXYGEN AND OF OXYGEN GAS

The oxygen probes are normally calibrated in either air or water saturated with air; the same readout is obtained in both cases. We have checked the probes in a pressure chamber filled with oxygen to certain pressures under two conditions: (a) for the gas only, where the probe is suspended in the chamber, with the only moisture present being that in the electrolyte solution within the probe, and (b) for water, where the beaker is placed in a beaker containing both water and a magnetic stirring bar. The results, shown in Tables IV and V, show that response of the probe in the gas is very rapid, within 1-2 minutes, but that the

response in water is much slower, probably due to the slow rate of solution of the gas in the water.

TABLE IV

RATE OF SOLUTION OF OXYGEN IN WATER

| Oxygen Pressure, psia | Readout, ppm | Time of Readout, min | |
|---|---|---|---|
| 15 (air) | 7.2 | -- | |
| 65 | 34 | 0 | |
| | 56 | 1 | |
| | 61 | 2 | |
| | 67 | 3 | |
| | 77 | 7 | |
| | 81 | 8 | |
| | 120 | 9 | (stirring increased) |
| | 130 | 10 | |
| | 130 | 16 | |
| 15 (oxygen) | 80 | 1 | (pressure relieved) |
| | 39 | 2 | |
| | 37 | 4 | |
| | 39 | 5 | |
| 65 | 57 | 1 | |
| | 75 | 2 | |
| | 91 | 3 | |
| | 110 | 4 | |
| | 115 | 5 | |
| | 120 | 6 | |
| | 125 | 7 | |
| | 130 | 8 | |
| | 132 | 9 | |
| 115 | 145 | 10 | |
| | 175 | 11 | |
| | 200 | 12 | |
| | 205 | 13 | |
| | 205 | 14 | |
| | 215 | 17 | |
| 15 (oxygen) | 32.5 | -- | |

Note: Initially the chamber was filled with air (0 psig or 15 psia); this has about 3 psia oxygen. Thereafter the chamber was filled, at 0 psig or 15 psia, with oxygen.

TABLE V

RESPONSE OF OXYGEN SENSOR TO GASEOUS OXYGEN

| Oxygen Pressure, psia | Readout, ppm | Time of Readout, min |
|---|---|---|
| 15 | 50 | -- |
| 60 | 100 | 1 |
| | 142 | 3 |
| | 149 | 4 |
| | 150 | 5 |
| 90 | 210 | 1 |
| | 218 | 2 |
| | 218 | 3 |
| | 218 | 4 |
| 120 | 265 | 1 |
| | 282 | 2 |
| | 290 | 3 |
| | 290 | 4 |
| 150 | 330 | 1 |
| | 347 | 2 |
| | 358 | 3 |
| | 360 | 4 |
| | 360 | 5 |
| | 363 | 6 |

Note: Zero intercept of the above data, for 0 psia, is 10 ppm. The sensor was suspended in the pressure chamber, with no water present. A constant readjustment of the temperature adjustment on the readout was needed, as the temperature increased with pressure increase. The pressure readings are those read on the gage (psig) with 15 lb/sq inch added for atmospheric pressure. psia = psig + 15.

Air calibration is a starting point for the probes. However, extrapolation of this setting to much higher concentrations is a rather extreme and risky business. Also, the calibration seems to shift as we move up in pressure and then down again. Again the increase in readout, while roughly linear (Fig. 13), is only about 70% of that predicted by the pressure change.

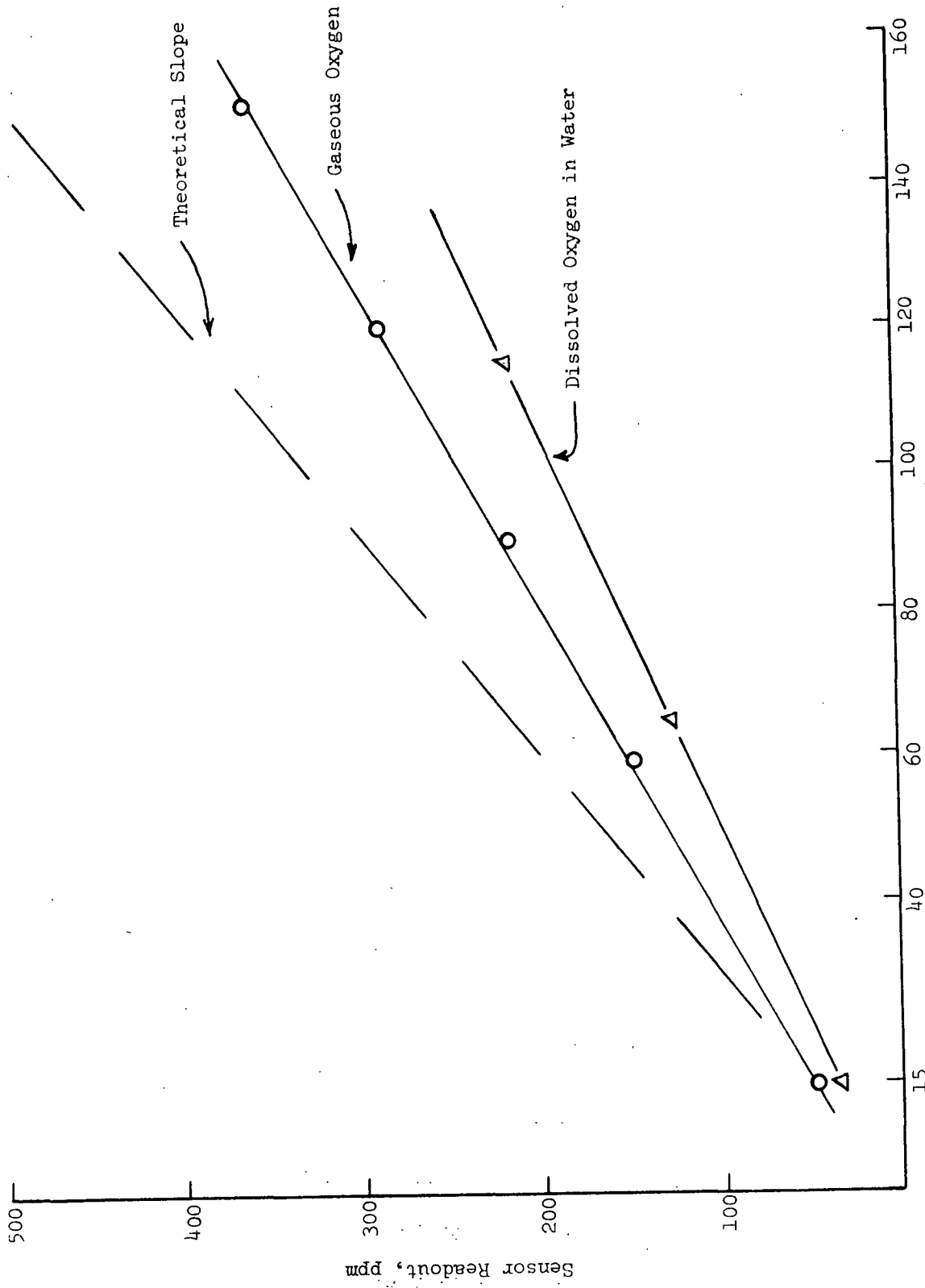



Figure 13. Linearity of Sensor Response

The rate of solution of oxygen in water is slow, but its removal from water when the pressure is relieved is much faster (see Table IV, change from 65 to 15 psia). We have tried to speed up the preparation of dissolved oxygen by increased stirring, and increasing the pressure to a high value, and then lowering it to the desired value.

Obviously more work is needed in working with these probes, and in their calibration by chemical means to confirm the electrical readouts. However, our main interest at present is in the rate of solution of oxygen in water, so that we can prepare dissolved oxygen solutions for use in our kinetic studies. Later we will consider the actual changes in dissolved oxygen concentration during a reaction; at present our main interest is in insuring that an excess of dissolved oxygen, relative to the carbohydrate substrate, is present.

CONTROL OF DISSOLVED OXYGEN BY NITROGEN PRESSURE

A solution of dissolved oxygen is prepared by applying an oxygen pressure to an aqueous solution; when this pressure is removed, the dissolved oxygen will bubble out of the solution. In the operation of the flow reactor it should be possible to pump such solutions through a system of coils without any loss of oxygen. We have been able to handle this problem by applying a nitrogen pressure to the end of the coils to keep oxygen gas (and liquid) from emerging from the coils prematurely.

Theoretically, the amount of oxygen in solution is proportional to the partial pressure of oxygen above the solution. Thus, our oxygen sensors show readings of about 8-10 ppm for one atmosphere of air at room temperature, but for one atmosphere of oxygen, where the partial pressure of oxygen is about 5 times that in air, the readout from the sensor is in the 40-50 ppm range. Also,

if we increase the oxygen pressure above the solution, the readout will rise accordingly. When the oxygen pressure is lowered again to one atmosphere, the readout will revert to the 40-50 ppm range.

Similarly, if we replace the oxygen atmosphere with the same pressure of nitrogen, the dissolved oxygen will rapidly bubble out of solution. Thus, we pumped a solution of dissolved oxygen (about 167 ppm) from one pressure chamber through the flow reactor into a second chamber containing nitrogen. When the solution reached the beaker in the second chamber, the oxygen probe there initially read about 100 ppm oxygen but the readout dropped rapidly as the oxygen bubbled out. This was because the partial pressure of oxygen in the second chamber was essentially zero (see Table VI).

TABLE VI

DISSOLVED OXYGEN SOLUTION IN A NITROGEN ATMOSPHERE

| Time, min | Oxygen Chamber (A) | | Nitrogen Chamber | |
|---|---|---|---|---|
| | psig | Oxygen, ppm | psig | Oxygen, ppm |
| 0 | 60 | 167 | 100 | 10-15 |
| 0.3 | | | 100 | 125 |
| 2.0 | | | 100 | 35 |
| 0 | 60 | 160 | 100 | 10-15 |
| 0.3 | | | 100 | 90 |
| 0.8 | | | 100 | 60 |
| 0 | 60 | 160 | 100 | 10-15 |
| 0.3 | | | 100 | 75 |
| 0.8 | | | 100 | 40 |

Note: The times recorded are those after the liquid in the syringe (see Fig. 2) is driven into the nitrogen chamber.

However, when the solution of dissolved oxygen is exposed only through the small end of a coil (about 0.006 sq inch cross section for 0.085 inch inside diameter) to a nitrogen pressure, the dissolved oxygen will not bubble out and there is no premature flow of liquid out of the coils caused by such bubbles. When the nitrogen flow is relieved, however, at the end of a kinetic run, then some extra liquid is forced out and is collected in a spill bottle.

We are not certain why the nitrogen acts as effectively as it does. It may be due to the small surface area at the end of the liquid column; the nitrogen pressure balances any pressure created by liquid being pushed out by emerging bubbles, and, thus, serves as a plug. Or it may be a capillary effect (11); the small surface may not be amenable to the escape of gas bubbles. In any case, oxygen gas does not escape, in contrast to the behavior when such solutions are exposed in a beaker with a large surface area.

This effect was checked quantitatively in two ways. First, as shown in Table VII, a given amount of dissolved oxygen solution was held in a syringe, attached with a coil to a receiver in a second chamber (see Fig. 14). The syringe holds 20.8 ml of liquid, and the coil and delivery line, both empty, have a volume of about 7 ml. Thus, the net volume to be delivered to the receiver in the second chamber should be about 13 ml. This was found to be so with zero pressure in both chambers. For an experiment with dissolved oxygen held under pressure, but with no pressure in the receiving chamber, a large volume of liquid was obtained, as some was forced out of the coil by escaping oxygen bubbles. When the second chamber was pressurized, the normal volume of liquid was obtained, showing no premature flow of liquid.

TABLE VII

FLOW OF SOLUTIONS CONTAINING DISSOLVED OXYGEN

| Original Solution, ppm dissolved oxygen | Chamber A | | Chamber B | | Liquid Collected, g |
|---|---|---|---|---|---|
| | Gas | Pressure, psig | Gas | Pressure, psig | |
| 8 | Air | 0 | Air | 0 | 13.190<br>13.230 |
| 130 | Oxygen | 50 | Air | 0 | 14.850<br>14.510 |
| 130 | Oxygen | 50 | Nitrogen | 100 | 13.170<br>13.290[a] |

[a]This sample of solution was held in the syringe, open to the coil and nitrogen in Chamber B, for 5 minutes. In the other experiments the solutions were pushed into B immediately after the syringe was filled from A.

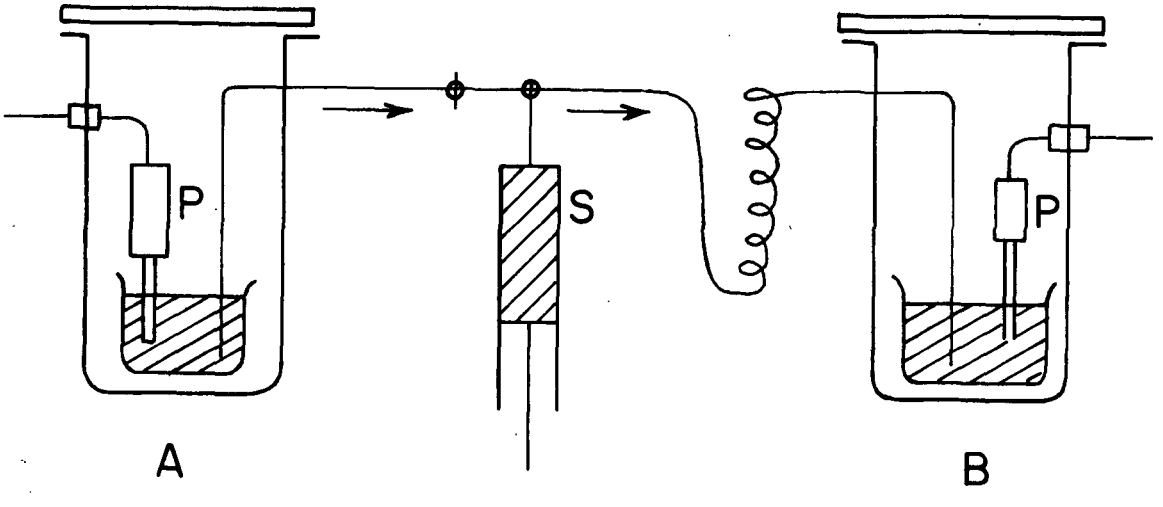



Figure 14. Movement of Dissolved Oxygen Into a Nitrogen Atmosphere

In the second experiment the complete flow reactor, with two heating coils and a reaction coil was used. One of the mix syringes contained 0.1N sodium hydroxide, and the amount of alkali in the quench bottle was titrated. This was about 6.5 ml, the predicted amount, and this volume of alkali was the same whether the heating coils were held at room temperature or whether they were heated to 120°C. The pressure in the oxygen chamber ($C_2$) was 135 psig, and that in the nitrogen chamber ($C_1$) was 150 psig. When the nitrogen pressure was relieved, about 10 ml of liquid was obtained in the spill bottle, showing bubble formation in the heating and reaction coils. (See Table VIII for calculated volumes.)

TABLE VIII

CALCULATED VOLUMES OF LIQUIDS IN HEATING AND REACTION COILS

| Volume of Various Components | Stage of Reactor Operation | | |
|---|---|---|---|
| | Syringes Filled | Heating Coils Filled | Reaction Run |
| 2 Mix syringes | 41.6 | 20.8 | 0 |
| Quench syringe | 100 | 100 | 0 |
| Heating coils | 0 | 20.8 | 25.5 |
| Reaction coil | 0 | 0 | 2.5 |
| Quench bottle | 0 | 0 | 113.6 |
| Total | 141.6 | 141.6 | 141.6 |

Note: After the reaction, when the nitrogen pressure is relieved, about 10 ml of liquid will be forced by emerging bubbles from the heating and reaction coils into the spill bottle. The total amount of solution from the two mix syringes found in the quench bottle is 13.6 ml (in addition to 100 ml from the quench syringe), or 6.8 ml from each syringe.

Hopefully this control of the dissolved oxygen will be verified by kinetic runs which will show good data and no discrepancies due to premature movement of liquid from the heating coils into the reaction coil.

# ANALYSIS OF CARBOHYDRATE SYSTEM

## INTRODUCTION

Very little has been published on the rates of attack of oxygen in alkali on simple carbohydrates. Most of the work has been a study of products and only a few experiments have been done on kinetics. The following paragraphs are a repetition of a section given in the original project proposal.

DeWilt and Kuster (11) studied the oxidation of glucose in 0.026N potassium hydroxide solution at 50°C and found a half-life of about 200 minutes. These investigators fed oxygen continuously into their system operated at atmospheric pressure, and employed an efficient stirrer to give an oxygen concentration of about 0.85 millimole per liter. An oxygen-analyzer sensing device was used to determine the oxygen concentration. The low concentration of oxygen inherent in the atmospheric studies of DeWilt and Kuster limits the application of their results to the problems of alkaline oxygen pulping.

Gleason and Barker (12) studied the rate of oxidation of pentose sugars in 0.833N potassium hydroxide solution at 25°C and found half-lives ranging from 500 to 1000 minutes. Reaction conditions for these studies comprised vigorous shaking, in a water bath, of the reaction flasks connected to an oxygen reservoir.

Although no kinetic studies have been reported on disaccharides such as cellobiose, or on oligosaccharides, several papers have been published on the isolation of products from alkali-oxygen systems performed in small digesters where the reaction time ranged from 30 minutes to many hours, and where the initial reactions were carried long beyond completion. Thus, Malinen, Sjostrom, and Ylijoki (13) carried out reactions with cellobiose in an autoclave at 120°C.

Heating to temperature required 20 minutes even though the cellobiose was completely reacted in 5 minutes. Samuelson and Thede (14) investigated the products of reaction of cellobiose in 18% sodium hydroxide solution and one atmosphere of oxygen at 25°C after a reaction time of 26 hours. Rowell (15) bubbled oxygen or air into solutions of cellobiose in 0.04N sodium hydroxide or barium hydroxide solutions and employed reaction times ranging from 48 hours at 25°C to 3 hours at 100°C. In all instances, conclusions as to the relative amounts of oxidation and peeling were derived from the yields of an eleven-carbon acid, 3-O-β-D-glucosyl-D-arabinonic acid, and from yields of isosaccharinic acid and other acids containing six carbons or less. It was generally agreed by these several investigators that more oxidation occurred at lower temperatures, and that more peeling occurred at higher temperatures. In addition, oxidation was favored by higher alkalinity and oxygen pressure (13). The major oxidation product, the eleven-carbon acid, was not stable at long reaction times of 2 hr in 1% sodium hydroxide solution at 120°C, whereas cellobionic acid, a minor oxidation product, was relatively stable.

Data on reaction rates of the four important carbohydrate reactions for alkaline oxygen systems are presented in Table IX in which half-lives for the reactions are tabulated to give the reader an idea of their relative rates (the slower the rate, the larger the half-life). The peeling reaction is very fast, and has been studied for alkaline systems in our flow reactor. The cleavage reaction, being extremely slow, has been studied in batch reactors and digesters. Only a limited amount of work has been performed on the other two reactions which are fast, and these studies were done only at lower temperatures.

TABLE IX

HALF-LIVES OF REACTIONS OF CELLOBIOSE IN ALKALI-OXYGEN SYSTEMS

| System | Peeling Reaction | Stopping Reaction | Oxidation Reaction | Cleavage Reaction |
|---|---|---|---|---|
| 2N Alkali at 170°C | 5-10 ms[a] | 1000 ms | None | 1800 min[b] |
| Similar, with oxygen | ? | ? | ? | 35 min |
| 0.02N Alkali at 60°C | 20 min | 500 min | None | Very slow |
| Same for glucose with oxygen at 50°C | Very slow | ? | 200 min | Very slow |

[a] ms = milliseconds.

[b] min = minutes.

Alkaline Peeling of End Groups

This is a very fast reaction, and the rate is proportional to the alkali concentration (up to 0.1N sodium hydroxide) and to the temperature (Fig. 15). This reaction is finally terminated in polysaccharides by a "stopping reaction" comprising a rearrangement of the carbonyl end group to an alkali-stable metasaccharinic acid. It is interesting to note that in their studies with glucose, DeWilt and Kuster (11) state that there is very little rearrangement of the sugar to saccharinic acids, and that the bulk of the reaction is oxidation. This would indicate that either the oxidation is much faster than rearrangement or that the rearrangement reaction is inhibited. We would like to check this work with a model disaccharide, cellobiose, to determine whether the main product will be a disaccharide acid or a peeling to two six-carbon units, and to determine whether we can slow down the rate of peeling.

Stopping Reaction

The rearrangement of the carbonyl end group to an alkali-stable metasaccharinic acid has received very little study. The rate of reaction has been

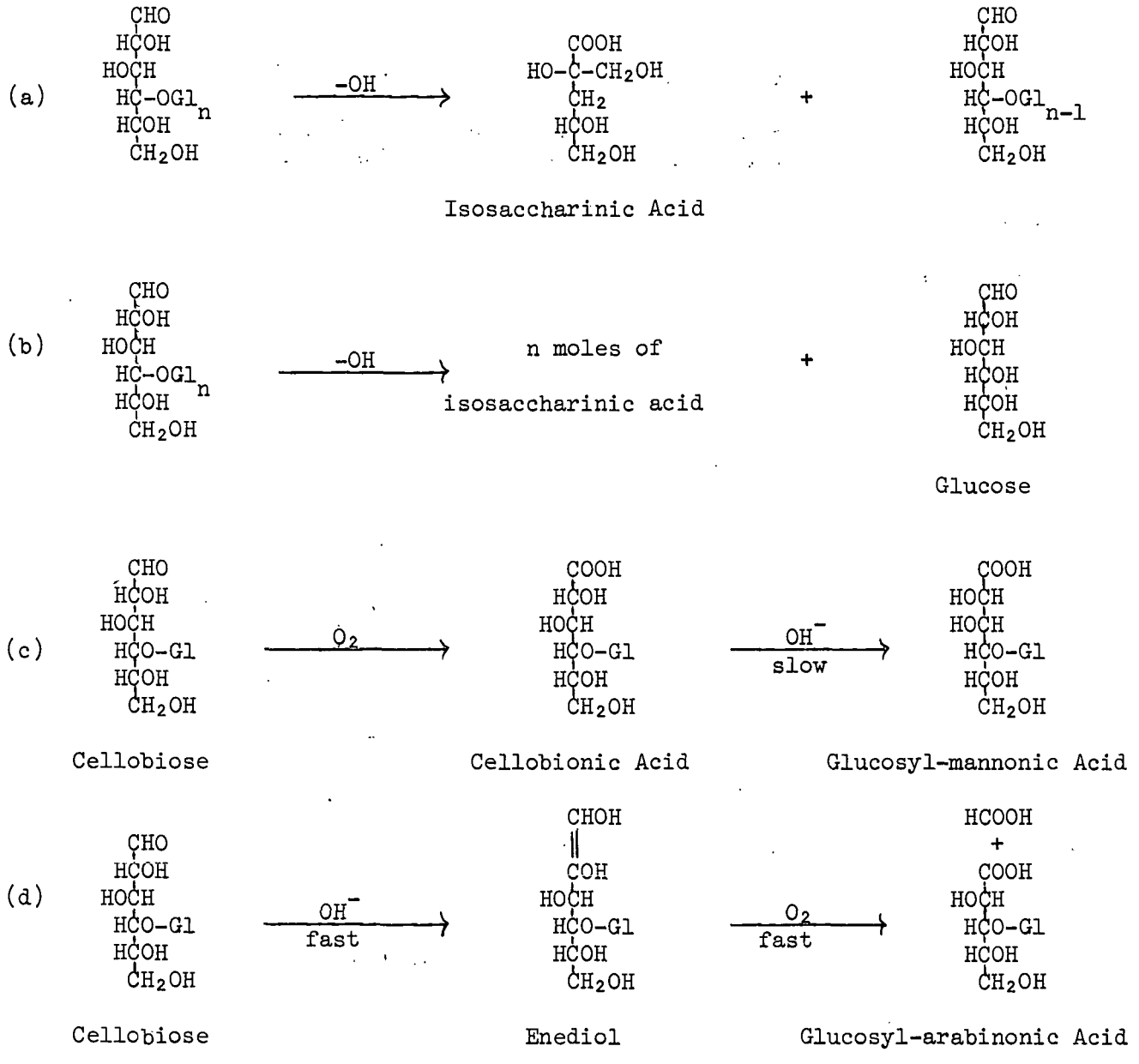



Figure 15. Reactions of Cellobiose in Alkali-Oxygen System (a) = Peeling, (c) and (d) Oxidation to C-12 and C-11 Acids. (b) = Peeling of Polysaccharide

estimated from the relative yields of products from peeling and from the stopping reaction in a system that has been carried to completion. This reaction involves the elimination of the hydroxyl group (a difficult leaving group) at carbon-3 rather than the glucosyl group (an easy leaving group) at carbon-4. Presumably (from evidence in the literature on simple sugars), in contrast to the competing peeling reaction, the stopping reaction should be favored by calcium ion and not by sodium ion, and also by lower temperatures. This reaction should be relatively unimportant compared to the oxidation reaction.

Oxidation Reaction

This reaction is concerned with the oxidation of the end group by molecular oxygen. To date, the rate of this reaction has been studied only with glucose (11) and was found to be slower than the peeling reaction under the same conditions. We would like to investigate the cellobiose model system to determine whether the oxidation reaction is a factor in polysaccharide reactions or whether the main attack of oxygen is on the glycosidic bonds. The end group oxidation reaction would be beneficial, but the glycosidic bond cleavage would be detrimental in pulp production (see Fig. 11).

Cleavage Reaction

This reaction of the breaking of glucosidic bonds between two units was investigated by Best and Green (16) who studied the model, methyl cellobioside. The cleavage reaction is a very slow reaction which is favored by higher temperatures and increased alkali concentration, and its occurrence in polysaccharides is followed by the very fast peeling reaction until the stopping reaction takes place. The cleavage reaction is accelerated greatly (about 50 times) by the presence of oxygen in the digester, and this acceleration has been attributed to initial attack on the hydroxyls adjacent to the glycosidic bond (17).

PROPOSED ANALYSIS BY GAS CHROMATOGRAPHY

Initially we are planning to determine two main components in the reaction systems obtained by the effect of alkali-oxygen on cellobiose. They are: (a) unreacted cellobiose, which we can correlate to a great extent with the rate of peeling, and (b) the C-11 and C-12 acids that are formed by oxidation. In Fig. 16 is shown a gas chromatogram of the products obtained by the limited oxidation of cellobiose in 0.1N sodium hydroxide for 24 hours at room temperature. There is a great amount of unreacted cellobiose left (about 75%), determined by its relationship to the internal standard used, perseitol. In Fig. 17 the gas chromatogram represents the same system, after the products had been treated with 0.1N sodium hydroxide at 90°C for one hour to remove unreacted cellobiose. Now we have two small peaks in the disaccharide region that may represent the C-11 and C-12 acids.

We will have to prepare these acids separately, but at present we were concerned with the quick determination of alkali-stable disaccharide products. We tried a relatively incomplete oxidation to insure that such oxidation products were obtained. Now we can apply this method to our flow reactor; we have been concerned about the possible nonformation of such products due to escape of oxygen from our flow reactor. With this type of chromatogram as a prototype, we will know what to look for in our flow reactor experiments.

The given reaction solution was worked up by treatment with Amberlite IR-120 resin to remove alkali, and concentrated to a small volume. This was divided into two portions. One was heated with 0.1N sodium hydroxide in a nitrogen atmosphere at 90°C for one hour, then cooled, and treated with IR-120 resin as above. Both solutions (pH about 3 to 3.5) were concentrated to small volumes, and aliquots representing 2-5 mg of the original cellobiose concentrated to dryness

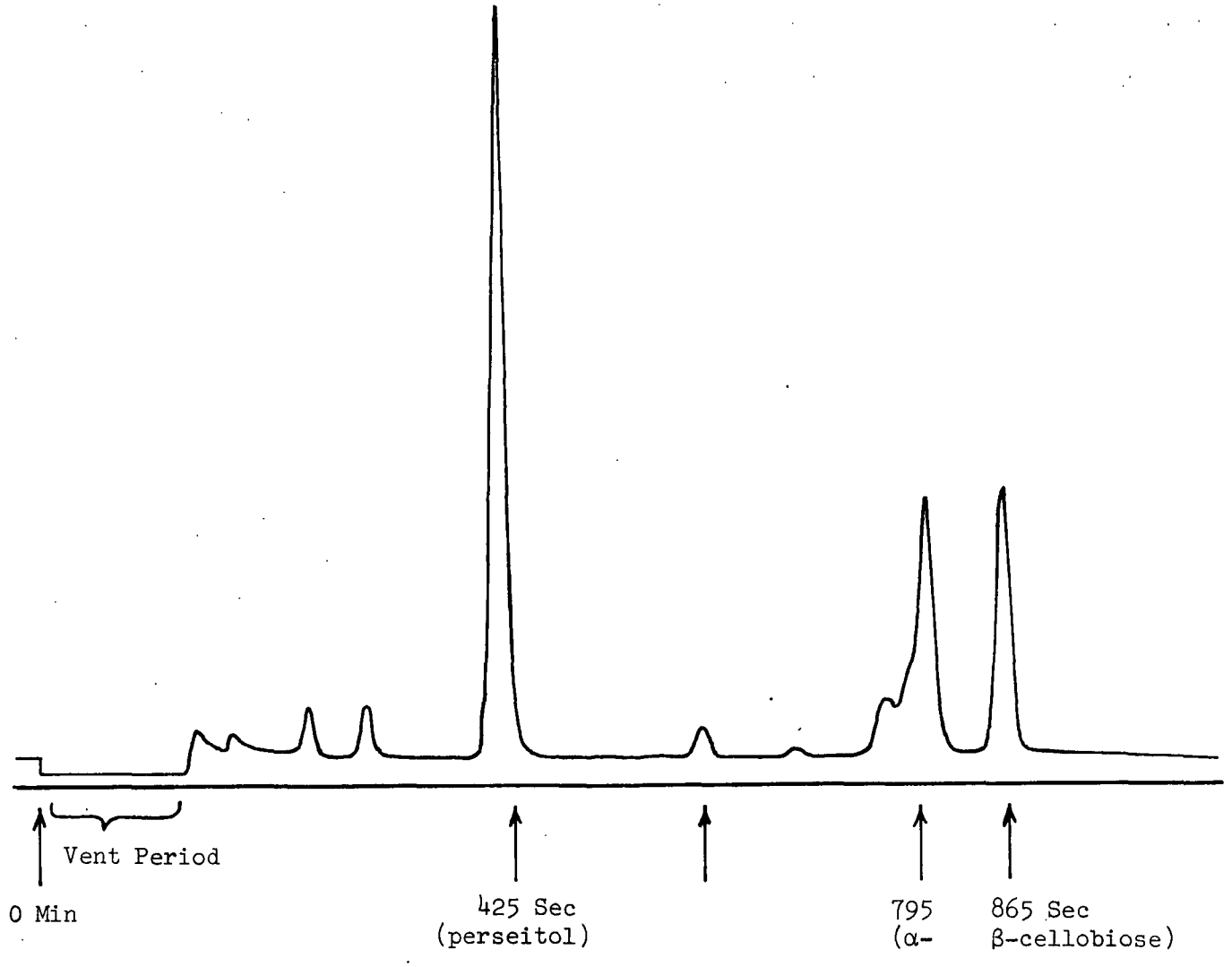



Figure 16. Gas Chromatogram

in 6-ml Hypo-vials (18). These were then dried for two hours *in vacuo* over phosphorus pentoxide, and then trimethylsilylated with TriSil Concentrate and dimethyl sulfoxide (18) by shaking at room temperature overnight. The vials were sealed with Disc-Teflon rubber laminated septa (18) and crimped aluminum caps before shaking; the septa did not react with the trimethylsilylating agent. The crimped caps were removed, the liquids transferred to 1-ml Reacti-vials (18), and portions (2-5 µl) of the upper layers injected on the gas chromatograph (6 ft x 1/8 inch OV-17 column, programmed from 160°C to 250°C at 6°/min, nitrogen

flow 15 ml/min). A Valco 4-port switching valve (19) was used to vent the initial trimethylsilylating agent for two minutes; this kept the detector from being fouled up with silica deposits. The peak times and areas were recorded with a Varian 485 digital printout integrator.

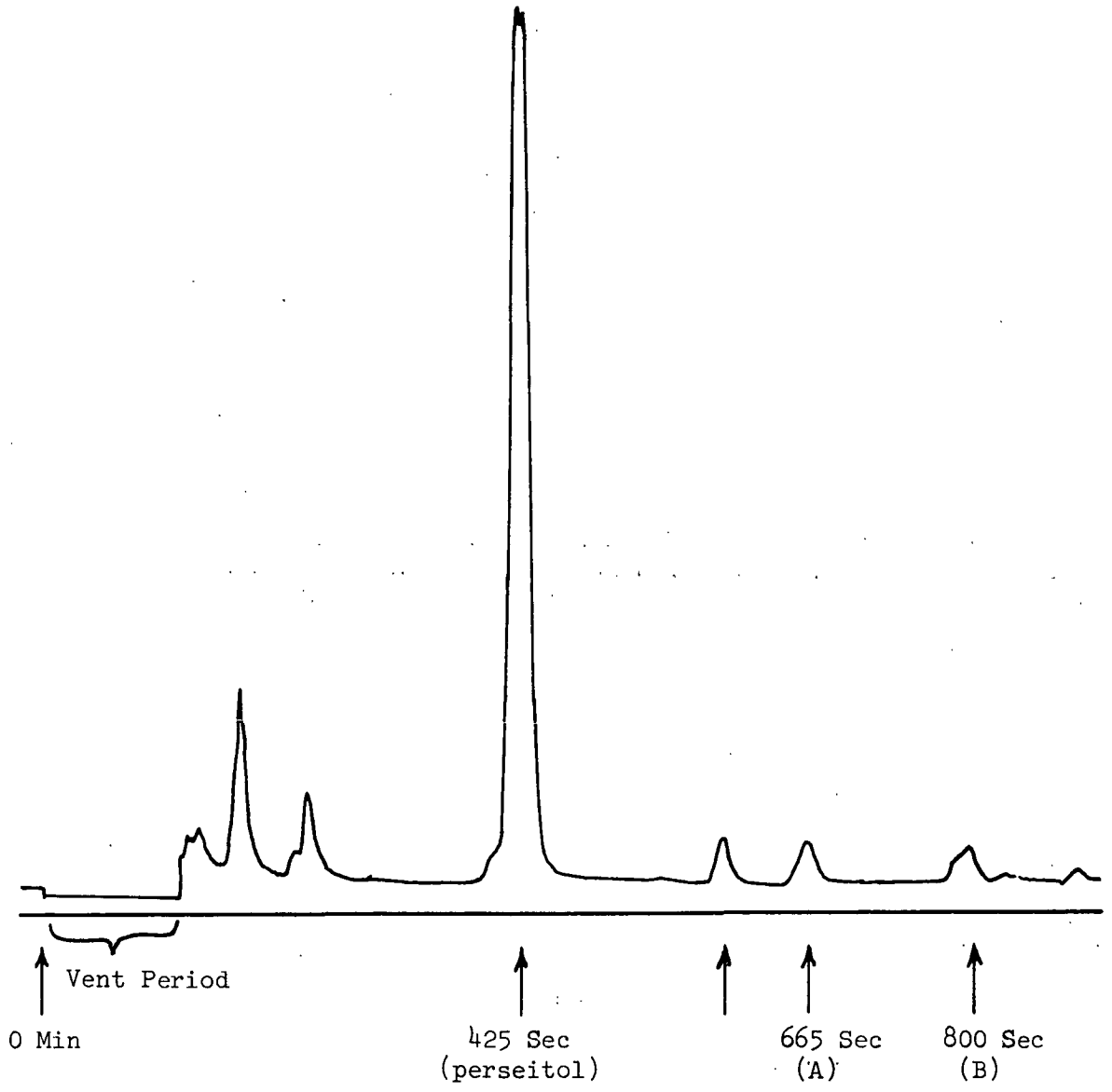



Figure 17. Gas Chromatogram

OXIDATION OF CELLOBIOSE BY OXYGEN IN 0.1N SODIUM HYDROXIDE

A solution of 136 mg cellobiose in 200 ml of 0.1N sodium hydroxide was placed in a pressure chamber, the latter pressurized to 135 psig oxygen, and the system left overnight. The system was relieved, a 1/5 aliquot treated with perseitol (20) as an internal standard (20.2 mg per 25.6 mg original cellobiose) and the system treated with IR-120 resin, etc.

This reaction was run in two manners. The first contained 10 mg magnesium sulfate and the second contained 10 mg cobaltous chloride. The sulfate ion was removed during the workup in the first method with barium hydroxide, the chloride in the second method was left in and was presumably removed as hydrogen chloride in the concentration of the solution to dryness in vacuo.

PEROXIDE FORMATION IN CARBOHYDRATE OXIDATION

According to Bamford and Collins (21) the reaction of glucose, and presumably all reducing sugars, in oxygen and alkali is not a radical reaction at room temperature and 85-200 mm mercury of oxygen. Although silver, cuprous, ferrous, manganous and cerous ions did not visibly affect the rate of reaction of oxygen with glucose, cobaltous ion and platinum black did so, but in different ways. Additives such as benzene diazonium hydroxide, benzoyl peroxide, sulfur, hydroquinone and picric acid confirmed the absence of radical reactions at room temperature. Bamford and Collins speculated that since peroxides were formed in uncatalyzed reactions and since negligible amounts of peroxides were detected when transition metal ions were present, these latter ions probably did alter the reaction mechanism in a subtle manner.

At a later date Sinkey (22) proved that hydrogen peroxide was formed during these and similar reactions, when he reacted glucose with sodium hydroxide

and oxygen (75 psig) at room temperature, and showed that no organic peroxides could be detected. The initial rate of reaction was not affected by the presence of ferrous or magnesium ions or sodium pyrophosphate, although the ultimate stability of the peroxide was affected. If this were the only behavior of reducing sugars with oxygen, the addition of hydrogen peroxide to oxygen bleaching reactions should be equivalent to adding glucose. Since Samuelson and Stolpe (23) found this not to be the case at elevated temperatures, it can be conjectured that complex mechanistic pathways are involved when aldoses are reacted with oxygen.

In general, radical autoxidation reactions are favored by temperatures greater than 100°C and it is anticipated from the research of McCloskey (24), Sinkey (22), and Weaver (25) that they occur under the conditions of oxygen pulping and bleaching. Since the yield of pulp after oxygenation reactions is unexpectedly high compared to kraft and soda pulps, these reactions may actually be beneficial as far as yield is concerned.

It was hoped to show, during the qualitative experiments necessary to make the flow reactor operational, that cellobiose produces hydrogen peroxide analogous to glucose when reacted with oxygen, that no organic peroxides are produced at room temperature, and that different product distributions occur when oxygen is present than in its absence. Other experiments were carried out comparing the qualitative differences between the noncatalyzed reactions and those reactions catalyzed by magnesium and cobaltous ions, to guide future research directions.

The results of this survey to date are shown in Table X and indicate that:

a. Hydrogen peroxide is the peroxide formed during the reaction with cellobiose.

TABLE X

PEROXIDE ANALYSIS WITH TITANIUM SULFATE

Experiments 1 and 2

68 mg cellobiose in 120 ml 0.1N sodium hydroxide, 135 psig oxygen, 18-20°C, and 24 hr reaction time.

| Experiment | Time of Peroxide Analysis, hr 1/6 | 4 | 24 |
|---|---|---|---|
| 1. Hydrogen peroxide found, mM/liter | 0.06[a] | 0.06 | 0.05 |
| | 0.06 | -- | -- |
| 2. Hydrogen peroxide found, mM/liter | 0.05 | 0.05 | 0.05 |

Experiment 3

No cellobiose, 120 ml 0.1N sodium hydroxide, 135 psig oxygen, 18-20°C, 24 hr reaction time.

Experiment 4

340 mg cellobiose in 100 ml 0.1N sodium hydroxide, 135 psig oxygen, 0.001M magnesium sulfate, 18-20°C, and 24 hr reaction time.

| Experiment | Time of Peroxide Analysis, hr 1/6 | 6 | 24 | 48 |
|---|---|---|---|---|
| 3. Hydrogen peroxide found, mM/liter | 0 | 0 | -- | -- |
| 4. Hydrogen peroxide found, mM/liter | 0.180[b] | 0.177 | 0.200 | 0.198 |

Experiment 5

136 mg cellobiose in 200 ml 0.1N sodium hydroxide, 135 psig oxygen, 0.0001M magnesium sulfate, 18-20°C, and 24 hr reaction time.

Experiment 6

136 mg cellobiose in 200 ml 0.1N sodium hydroxide, 135 psig oxygen, 0.0001M cobaltous chloride, 18-20°C, and 24 hr reaction time.

| Experiment | Time of Peroxide Analysis, hr 1 | 24 |
|---|---|---|
| 5. Hydrogen peroxide found, mM/liter | 0.09[b] | 0.10 |
| 6. Hydrogen peroxide found, mM/liter | 0.02 | 0.02 |

[a] Yield of hydrogen peroxide = 1.3% on cellobiose used.
[b] Yield of hydrogen peroxide = 1.8% based on cellobiose used.

b. No organic peroxides were detected when the reaction was carried out at room temperature.

c. Magnesium ion stabilizes the hydrogen peroxide formed in the reaction.

d. Cobaltous ion decreases the hydrogen peroxide detected; no organic peroxides were detected in the presence of this ion.

e. The low levels of peroxide formation (expected) suggest that alternative quenching techniques must be employed if hydrogen peroxide is to be measured during anticipated future research.

f. Gas chromatographic data suggest small but real differences in reaction mechanisms between catalyzed and noncatalyzed reactions.

# THE EFFECT OF TRANSITION METALS* ON THE REACTION OF OXYGEN WITH ALKALINE SOLUTIONS OF GLYCOSIDES

## INTRODUCTION

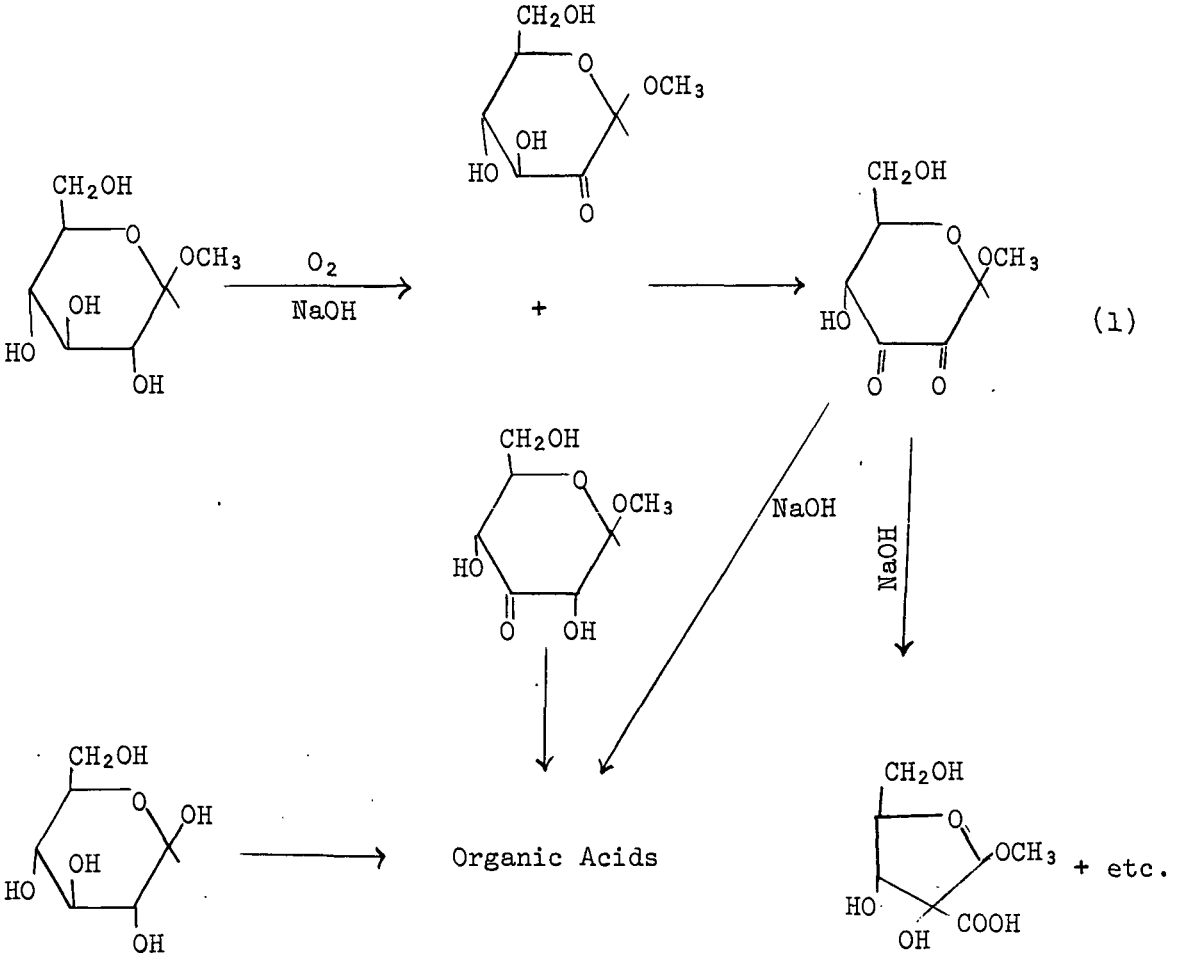
Because of the known catalytic effect of transition metals and their ions on oxygenation reactions of all types (26), it was concluded that the high surface area to volume ratio of stainless steel used in a flow reactor would lead to different results than those obtained from commercial pulping installations with their relatively low surface area to volume ratios. Since the necessary kinetic versatility could not be achieved using other designs incorporating a low surface to volume ratio, it was necessary to change the materials of construction of the existing apparatus design.

## METHOD

The experimental technique necessary for testing metals for their catalytic influence must be capable of predicting the performance during the reaction of carbonyl groups of reducing sugars with oxygen. The apparently simpler procedure of testing the effect of reducing sugars themselves was ruled out since the only apparatus capable of handling the reaction was the flow reactor which was being redesigned. An alternative evaluation could be achieved by subjecting test strips of metal to chemical environments in a pressure vessel constructed of Teflon. As mentioned above, the rapidity of the reaction of oxygen and alkali with reducing sugars and the inability to measure the reactants during their short life time made their use impossible in this apparatus.

*These metals constitute groups of elements in the fourth, fifth, and sixth periods of the periodic table that have characteristic electron distributions in their outer shells. Those metals of use in fabrication have been examined in this report. Ordinarily, only those elements or their ions of atomic numbers 21 to 30 are of significance to the pulp and paper industry.

Instead, it was conjectured that the evaluation could be conducted more conveniently and inexpensively by reacting methyl glucosides with oxygen and alkali in the presence and absence of test metal strips. Although the glucosides do not initially resemble reducing sugars and, therefore, might not be considered satisfactory models because of the absence of an aldehydic group, their degradation products do go through carbonyl intermediates (27). These ketonic groups are conjectured to go through several reactions, one of which is analogous to the reaction of aldoses with alkali:



The presence of transition metals and their ions should affect the postulated mono- and diketo intermediates in a manner similar to their effect on the aldehydic groups of reducing sugars. These reactions will be further complicated, though in similar fashions, by the formation of intermediate hydrogen peroxide from the reaction of aldoses and oxygen (22,28) and of glycosides and oxygen (22,29). The catalytic influence of the transition metal ions on the resulting hydrogen peroxide will lead to the formation of hydroxyl radicals according to the well-known Haber-Weiss reaction (30). The effect of the transition metal ions will be reflected in a disappearance of hydrogen peroxide from

$$Me^{n} + H_2O_2 \longrightarrow Me^{n+1} + \cdot OH + OH^{-} \qquad (2)$$

$$Me^{n+1} + H_2O_2 \longrightarrow Me^{n} + \frac{1}{2} O_2 + H_2O \qquad (3)$$

the reaction mixture, the appearance of organic peroxides (31) and an increased destruction of glycosides (GH) by the oxidative radicals derived from peroxide decomposition (32),

$$GH + \cdot OH \longrightarrow G\cdot + H_2O \qquad (4)$$

The effect of transition metals themselves in this reaction, in the absence of their ions, has never been observed since any supposed influence might also be due to traces of the dissolved ionic species. Some research has been conducted on the catalytic influence of various solid metals and oxides on peroxide decompositions and shown to be related to surface effects.

However, it can be assumed that a measure of the loss of glycoside and the formation of hydrogen peroxide and organic peroxides will be an indication of the catalytic activity of any additive and its ions to a reaction when compared to a control although the mechanism cannot be formulated. The organic

peroxides formed during the reaction do depend upon the transition metal ions to catalyze a termination reaction first observed by Karasch and Fono (33)

$$GOO\cdot + R\cdot \xrightarrow{Me^{n}} GOOR \qquad (5)$$

It is possible that the transition metals and their ions might have a unique effect on aldehydic carbonyls that they do not have upon ketonic carbonyls. However, those metals that do affect the degradation of glycosides will also affect the degradation of aldoses in a similar manner. Thus, the test can eliminate most possibilities but cannot predict with absolute certainty the noncatalytic influence of presumably inoccuous metals on the reaction of aldoses. This can be done only with a modified flow reactor.

EXPERIMENTAL

The apparatus used for this investigation was the Teflon-lined 1-liter reactor designed by McCloskey (24) and Sinkey (22). It was operated in the manner described elsewhere (34). Test metal strips purchased from Ventron Corp. cut to 1 x 6 inches, were attached to the Teflon baffle within the reactor. Methyl-α-D-glucopyranoside, and in a few instances methyl-β-D-glucopyranoside, was reacted with 5% sodium hydroxide and 100 psig oxygen at 120°C for different times in the reactor with the strips present. The reaction was quenched by cooling and the contents analyzed for unreacted glycoside by gas chromatography (24). Peroxide analyses for both hydrogen peroxide and organic peroxides were carried out using conventional techniques (11), and the dissolved metal contents of the liquors were measured by flame photometry.

The stability of alkaline peroxide solutions to certain of these metals at room temperature was also tested by adding the metal strips in their Teflon

holders to a stirred alkaline peroxide solution composed of 500 ml triply distilled water, 25 g NaOH, and 1 ml of 14% $H_2O_2$. Samples were removed at periodic intervals for peroxide analysis (see Table IX).

Before testing, all metals were soaked in water and organic solvents in an attempt to remove soluble surface impurities. Several metals such as vanadium and molybdenum developed highly colored oxides on their surfaces during the water treatment and consequently were not evaluated further, since it was feared they would corrode severely in alkali. Others, such as chromium, niobium and tantalum were available if none of the first testing series proved acceptable.

The metals finally chosen for evaluation were stainless steel (No. 316), nickel, cobalt, titanium, tungsten, zirconium, platinum and silver. Following reaction, the alkaline solutions were analyzed for dissolved metals. The control solution contained 5.9 ppm iron, 2.1 ppm aluminum, and 0.69 ppm copper introduced from impurities in the reagent grade caustic.

RESULTS

The data plotted in Fig. 18 compare the amount of hydrogen peroxide formed when methyl α-D-glucopyranoside is reacted for different times under standard conditions in the presence of various metals with the reaction in their absence. It is conjectured that the production of hydrogen peroxide is not affected by the metals (not proven), but that its subsequent decomposition is catalyzed to different extents by either the metals themselves or their ions in solution. A critical examination of the different shapes of the peroxide concentration curves formed in the presence of metals to that of control indicates that all these metals do affect the reaction to different extents. The stabilization of peroxide by tungsten metal indicates it to be as effective as magnesium

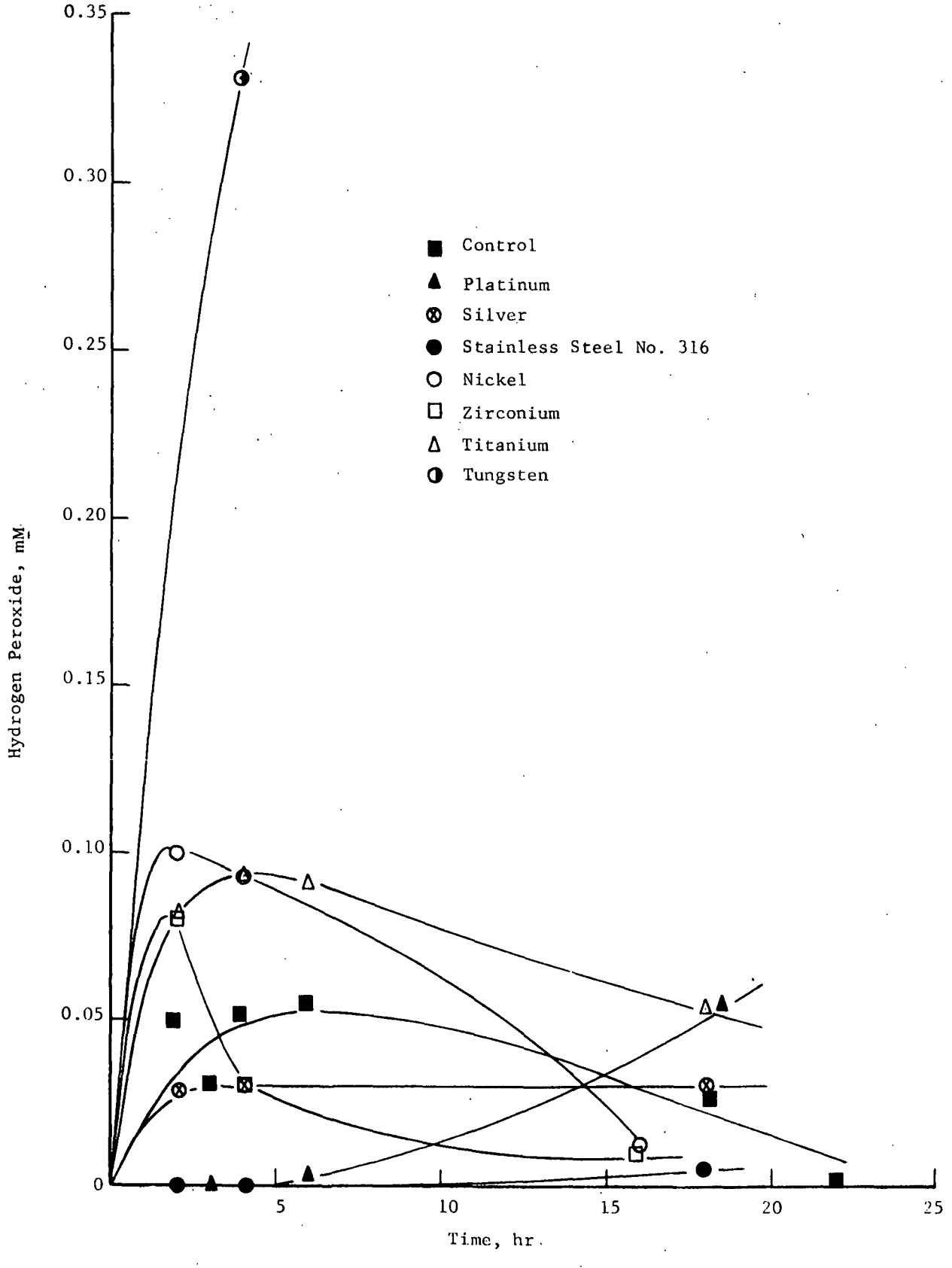



Figure 18. The Production of Hydrogen Peroxide from the Reaction of Methyl-α-D-glucopyranoside with Oxygen and Alkali in the Presence of Different Metals

ion (not shown), and the high solubility of the former metal in alkali (apparent only after acidification) suggests it is sodium tungstate rather than the metal itself which is the effective compound. Stainless steel causes an inhibition of peroxide formation characteristic of the iron and chromium salts that have gone into solution during the reaction. The production of hydrogen peroxide during the reaction in the presence of nickel, zirconium, titanium and silver resembles that of the control more closely than does the hydrogen peroxide formations in the presence of the other metals.

The results summarized in Fig. 19 demonstrate that silver, tungsten, cobalt and stainless steel catalyze the formation of more organic peroxide than does the control. These results suggest the metals or their ions which are in solution catalyze a Karasch and Fono (33) type dialkyl peroxide synthesis or termination reaction (see Reaction 5). Whether or not glycoside degradation also occurs depends not on this termination reaction but on the ratio of the propagating to all types of termination reactions catalyzed by the metals or their salts. Thus, the production of stable organic peroxide is not necessarily a measure of glycoside degradation, but does indicate the occurrence of different equilibria of consecutive, competing and terminating reactions.

Nickel, zirconium and titanium do not appear to influence this dialkyl peroxide termination reaction to a greater extent than the control. Thus, the observed termination reactions will likely be related to the presence of peroxyl radicals and organic radicals and to the catalytic influence of the small amount of iron in the control solutions and not to the three metals being discussed. Platinum and silver influence the reactions in an anomalous manner, and it is hoped that an explanation of these interesting behaviors may be found in the vast amount of literature dealing with the catalytic effects of these two metals in a variety of reactions.

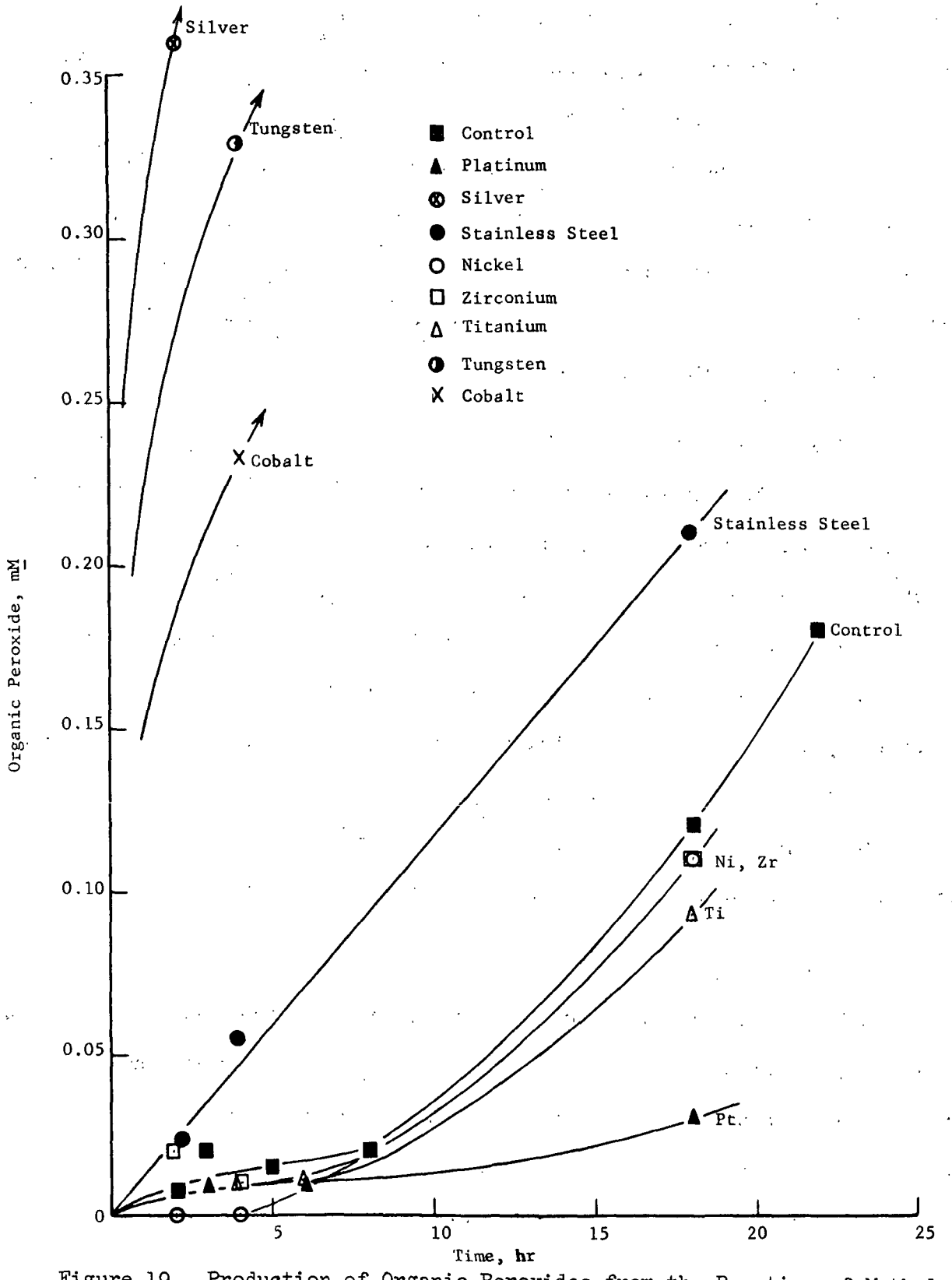



Figure 19. Production of Organic Peroxides from the Reaction of Methyl-α-D-glucopyranoside with Oxygen and Alkali in the Presence of Different Metals

The behavior of nickel and zirconium metals during the degradation of methyl-β-D-glucopyranoside was studied to see if the β-glycosidic configuration would react differently than did the α-configuration. The results are shown in Fig. 20. Once again the presence of neither metal affected the production of hydrogen peroxide significantly and was, therefore, similar to the control in this respect. The effect of nickel (as was shown above for methyl-α-D-glucopyranoside) on the formation of organic peroxides was identical to the control whereas zirconium metal significantly enhanced the formation of the organic peroxides. The results suggest that special effects due to the relative spatial characteristics of the glycosides, the surface of metals, and the shape of their ions may exist to a small degree.

The data plotted in Fig. 21 compare the effect of various metals on the degradation of methyl-α-D-glucopyranoside itself during the reaction with 100 psig oxygen, at 120°C and 5% NaOH. The glycoside is degraded at about the same rate as the control reaction when the reaction is conducted in the presence of nickel metal and possibly also in the presence of titanium metal. In the interest of brevity, the effects of other known harmful metals and metal ions were not investigated. The effect of cobalt on one reaction was analyzed as an example to show the type of results to be expected from these harmful metals on the degradation of glycosidic bonds. Less is known of the stabilizing action (indicated by the induction period) of zirconium and platinum metal during the reactions, but the effect is similar to that exhibited by magnesium ion in which an induction period occurs before the onset of the bond degradation. The different ratios of peroxides in these cases suggest that platinum metal, after the induction period, catalyzes a rate of reaction approximating that of the unstabilized system. The behavior of titanium has not been reported previously, and the metal

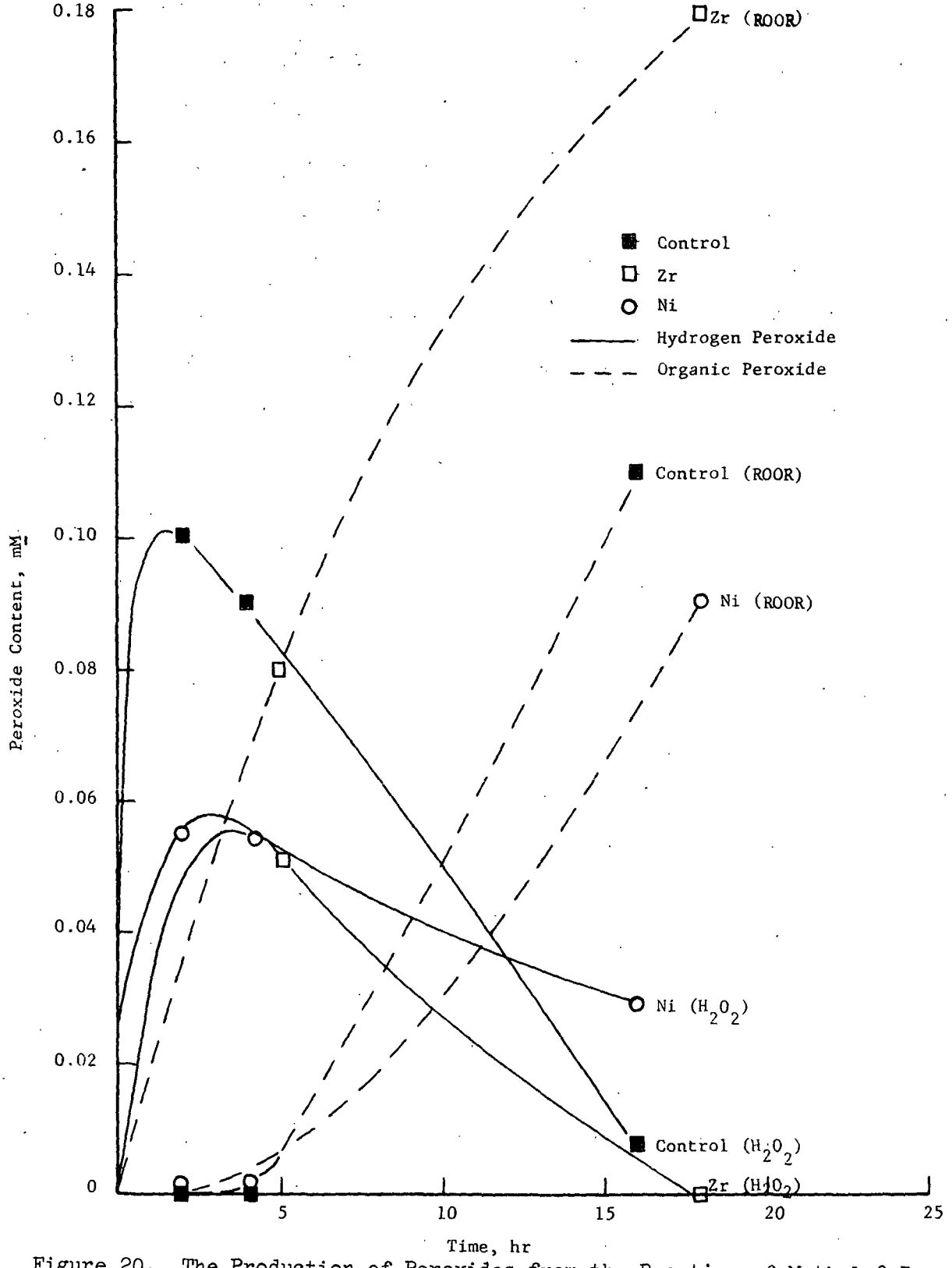



Figure 20. The Production of Peroxides from the Reaction of Methyl-β-D-glucopyranoside with Oxygen and Alkali in the Presence of Different Metals

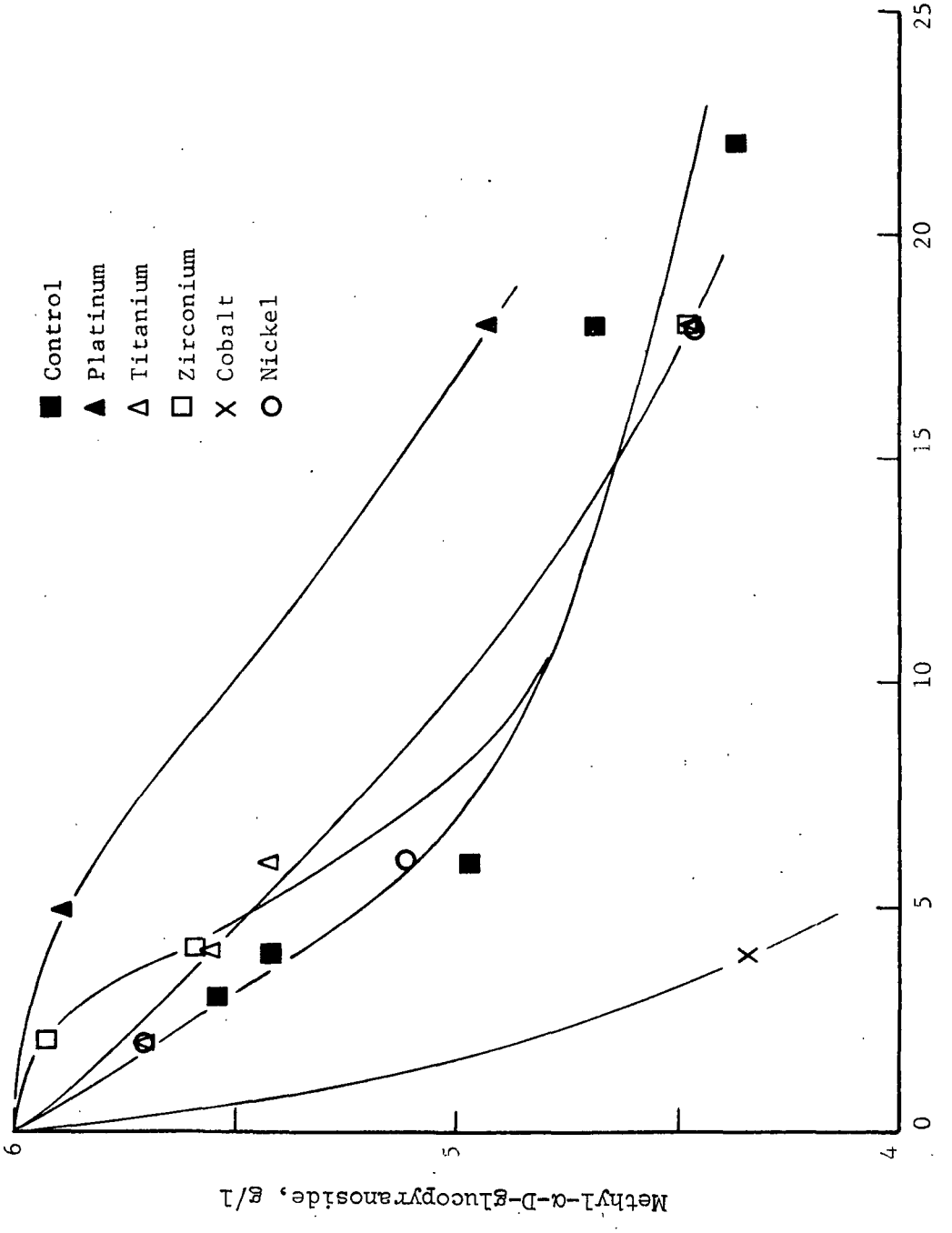



Figure 21. The Loss of Methyl-α-D-glucopyranoside During Reaction with Oxygen and Alkali in the Presence of Different Metal Strips

(as will be seen later) was extensively dissolved by the alkaline oxygen solutions. Thus, titanium salts may contribute to the observed behavior. The results indicate that the oxidation of the titanium must favor the $Ti^{+4}$ valence since the $Ti^{+3}$ valence is a known radical initiator in the presence of peroxide (35), in a manner similar to $Co^{+2}$, $Fe^{+2}$, $Cu^{+1}$ and $Cr^{+1}$. In all likelihood, Reaction (6) predominates over Reaction (2) and effectively removes any lower valence titanous ion produced by Reaction (3). The alkaline conditions eliminate the possibility of the unique $Ti^{+4}$ reactions with hydrogen peroxide [Reaction (7)] contributing

$$Ti^{+3} \xrightarrow{O_2} Ti^{+4} \qquad (6)$$

$$Ti^{+4} + H_2O_2 \underset{k_1}{\overset{k_2}{\rightleftharpoons}} (Ti^{+4} \cdots H_2O_2) \longrightarrow \text{paramagnetic species S1, S2} \qquad (7)$$

to the system (36).

The neutral influence of nickel in oxygen-alkali reactions observed (37,38) here is much more controversial. The early literature indicates that $Ni^{+2}$ added to viscose aging processes accelerates cellulose degradation relative to other ions in the orders shown below:

$$Fe > Ni > Cu$$

$$Fe > Cu \gtrsim Ni > Mn$$

It might be postulated that the potential effect of nickel ion was minimized by the inertness of nickel metal to oxygen and the low solubility of its hydroxide. Consequently, insufficient nickel ion might be present to give results similar to those reported in viscose aging. However, this behavior of the nickel ion has not been observed during recent high temperature oxygen-alkali pulping and bleaching reactions. Landucci and Sanyer (39) found nickel ion adversely affected the rate of delignification during oxygen pulping, but it did not affect the degradation

of cellulose, i.e., the viscosity and carbohydrate yield of the pulp corresponded to the control. Rapson and coworkers (40) demonstrated nickel ion had no effect on pulp viscosity when added to an oxygen bleaching system. Although it is tempting to attribute these differences reported in the literature to the use of impure reagents by earlier workers, it is more likely that the difference is due to the inability of the nickelous ion to exist in the more powerful conditions of oxygen pulping and bleaching. Thus, for nickel ions as well as for titanium ions, the reaction generalized by Reaction (8) is overwhelmingly greater than Reactions (2) and (3) under the conditions of oxygen bleaching, but not under the conditions of cellulose aging.

$$M^{+1} \xrightarrow{O_2} M^{+2} \qquad (8)$$

The catalytic behavior of nickel sulfate +2, zirconium sulfate +4, and titanium sulfate +4 was determined in a separate series of experiments analogous to those reported elsewhere (39) in the Sinkey Reactor. The concentrations of the salts (0.05 mM) were greatly in excess of those derived from the metals. Nickel and titanium salts have a slight stabilizing action on hydrogen peroxide concentration whereas zirconium salts do not influence the concentration of hydrogen peroxide at all.

The production of organic peroxides is slightly less than that which occurs in the control. The low solubility of both nickel and zirconium metals in oxygen and alkali, coupled with the different effects of the metal and the salts on the degradations, suggests different catalytic effects are manifested by the metals and their salts. Although the change in glycoside concentration was not measured, the results suggest that the overall effect of nickel salts is not one of increased catalytic degradation as the earlier literature suggests,

but one of inertness or slight stabilization as the more recent literature demonstrates.

A summary of the effect of the metals on the oxygenation reactions studied here is given in Table VII together with the very limited data available in the literature. In general, the effect of the periodic group predominates except in the ambiguous case of the very complex Group VIII elements. Alloys composed of the less active metals may combine satisfactory chemical, physical and economic factors.

TABLE VII

THE RELATIVE BEHAVIOR OF ELEMENTS DURING ALKALINE OXYGENATION REACTIONS

| Periodic Group | IVB | VB | VIB | VIIB | | VIII | | IB |
|---|---|---|---|---|---|---|---|---|
| Element and effect in oxygenation reactions | Ti-22[a] (inert) | V-23 (corroded) | Cr-24 (mildly degradative) | Mn-25 (ambivalent) | Fe-26 (bad) | Co-27 (bad) | Ni-28 (inert) | Cu-29 (bad) |
| | Zr-40 (inert) | | Mo-42 (corroded) | | | | | Ag-47 (bad) |
| | | Ta-73 (corroded) | W-74 (stabilizes) | | Os-76 (corroded) | | Pt-78 (stabilizes) | |

[a]Element symbol and atomic number.

The ionic composition of the oxygenated solutions after reaction was determined by emission spectroscopy and the results suffered from the inherent lack of precision of that technique. The error in the determinations was further complicated by the fact that the impurities contributed by the sodium hydroxide, as well as those used to prepare the sample for analysis, were comparable in magnitude to those introduced by test samples. The results are summarized in Table VIII

and indicated that stainless steel is corroded by the alkaline medium while nickel and zirconium appear to be the most resistant. The occurrence of iron salts in solution after a reaction with a titanium strip probably occured as a result of desorption of iron salts from the Teflon walls of the reactor. A second test with titanium after the reactor had been properly cleaned, showed no iron in the oxygenated liquors.

TABLE VIII

THE COMPOSITION OF OXYGENATED LIQUORS AFTER REACTION IN THE PRESENCE OF VARIOUS METAL STRIPS[a] OF METHYL α-D-GLUCOPYRANOSIDE WITH OXYGEN AND ALKALI

| Test Sample | Mineral Content[a], ppm | | | | | | |
|---|---|---|---|---|---|---|---|
| | Fe | Al | Cu | Pt | Ti | Ni | Zr |
| Control | 5.6 | 2.3 | 0.75 | -- | -- | -- | -- |
| Platinum | -- | -- | -- | 10 | -- | -- | -- |
| Stainless steel, 316 | 7.0 | 0.7 | 0.2 | -- | -- | -- | -- |
| Titanium | 1.6 | -- | -- | -- | 11.3 | -- | -- |
| Nickel | -- | -- | -- | -- | -- | -- | -- |
| Zirconium | -- | -- | -- | -- | -- | -- | -- |
| Titanium[b] | -- | -- | -- | -- | 13.6 | -- | -- |
| Control | 6.1 | 2.0 | 0.65 | -- | -- | -- | -- |

[a]The metal ion contents of the test solution do not include the composition of the controls.

[b]The composition of ions from the reaction of methyl-β-D-glucopyranoside.

The effect of metals on the decomposition of hydrogen peroxide was also determined since it was reasoned that this would reflect the action of the metal on the various peroxides formed during the oxygen-alkali reactions. The results are summarized in Table IX and show that tungsten, and magnesium have powerful stabilizing actions. The stabilizing effect of nickel is marginal whereas zirconium has no apparent influence on the amount of hydrogen peroxide decomposed in 21 hours. Platinum and silver decompose alkaline peroxide solutions, but their contrasting effect upon glycoside degradation demonstrates that other deep-seated differences exist in addition to this similarity. Iron also decomposes peroxide and it is impossible to separate the effect of the metal itself from the effect of the salt.

## CONCLUSIONS

These results indicate that of the metals tested, nickel, titanium and zirconium have the least effect on the degradation of hydrogen peroxide or methyl glucosides in alkali and oxygen at 120°C. Other metals have either a stabilizing or a degradative effect on these reactants and would, therefore, affect the degradation of aldoses under similar experimental conditions. It is likely, therefore, that the three metals, and nickel in particular, will not affect the degradation of aldoses and will make suitable metals for the construction of certain specialized reactors.

TABLE IX

THE EFFECT OF METAL STRIPS ON HYDROGEN PEROXIDE DECOMPOSITION AND THE METAL ION COMPOSITION OF THE PEROXIDIC SOLUTION

| Metal Tested | Stainless Steel, 316 | Platinum | Silver | Nickel | Titanium | Zirconium | Tungsten | Magnesium | Control |
|---|---|---|---|---|---|---|---|---|---|
| $H_2O_2$ Remaining after 24 hr, % | 72.6 | 30.3 | 31.5 | 88.0 | 87.0 | 87.0 | 100 | 99.6 | 86.5 |
| Composition of liquors, ppm | | | | | | | | | |
| Iron | 0.7 | 1.5 | 0 | 0.1 | 0 | 0.4 | -- | -- | 5.6 |
| Aluminum | -- | 0.2 | 4.3 | 0 | 0.7 | 0.5 | -- | -- | 2.3 |
| Copper | -- | -- | -- | -- | 0.1 | -- | -- | -- | 0.75 |
| Silver | -- | 1.8 | -- | -- | -- | -- | -- | -- | -- |
| Chromium | 12.0 | -- | -- | -- | -- | -- | -- | -- | -- |

## FUTURE WORK

Now that the problem of controlling dissolved oxygen in the flow reactor seems to be solved, we will begin to make kinetic runs. We will use the conditions given below; these were given in the original project proposal. Our substrate initially will be cellobiose; it is readily available and is easily soluble in alkali. As the project continues, we will shift to other oligosaccharides and possibly hemicelluloses that can be handled as soluble systems. In all cases we will use small concentrations of substrate initially, so that dissolved oxygen is in molar excess.

Temperatures will be varied from 50° up to 120°C with emphasis on conditions where oxidation is at a maximum. From the studies in the literature already noted, we can expect greatest oxidation at lower temperatures. Alkali concentration will also be varied. Apparently, peeling is not increased in rate above a concentration of 0.1N (41). This is still a high pH. Therefore, in order to study oxidations at lower pH values of 8 to 9, we will employ buffer systems, probably mixtures of sodium carbonate and sodium bicarbonate. In all cases, an excess of alkali or buffer will be used, so that its concentration will not vary appreciably during the reaction. In addition, the use of catalytic ions of the transition metal type will be investigated. These ions may accelerate the desired oxidation, but they may also accelerate the decomposition of the products, such as the eleven-carbon acid.

## GLOSSARY

Dissolved oxygen — gaseous oxygen that has been dissolved either in water or in an electrolyte solution

ppm Dissolved oxygen — this ranges from about 8 ppm for air-saturated water up to 400 ppm in this work. 1 ppm = 0.000312 molar concentration.

Flow reactor — a device for studying short reaction times, by continuously pushing reactants through a reaction zone, with rapid mixing to start and stop the reaction

Position potentiometer — a device where the linear movement of a rod is transferred into electrical signals that are monitored on a switchboard

psia — the pressure applied to a system, in pounds per square inch; this includes 15 pounds for atmospheric pressure; psia = psig + 15

psig — the pressure read on a pressure gage in pounds per square inch; the gage reads zero at atmospheric pressure (15 lb/sq inch)

Quenching — the stopping of a reaction by either adding a reagent to neutralize one of the reactants, as acid to lower the pH of an alkaline solution, or adding cold water to lower the reaction temperature

## ACKNOWLEDGMENTS

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THE INSTITUTE OF PAPER CHEMISTRY

John W. Green
Senior Research Associate

Norman S. Thompson
Senior Research Associate

Irwin A. Pearl
Group Leader

John W. Swanson
Director
Division of Natural
Materials & Systems